

# THE DETERMINATION OF THE TOTAL OXYGEN CONTENT OF ORGANIC MATERIALS BY NEUTRON ACTIVATION

By

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## INTRODUCTION

Although oxygen in elementary or combined form is one of the most commonly occurring constituents of organic materials and its direct determination has been the subject of extensive investigation, the development and application of rapid instrumental methods have not kept pace with existing requirements.

Prior to 1939, methods for direct determination of oxygen in organic compounds were based on either complete oxidation of the compound with measurement of the oxygen consumed or catalytic hydrogenation (1) to form water. Both of these techniques were cumbersome, required complex apparatus, and were excessively tedious and time consuming. Neither could be considered amenable to routine application.

In 1939, Schutze (2) proposed a semi-micromethod in which the sample is thermally decomposed in a stream of nitrogen and the cracked products are passed over carbon at about 1000°C. The resulting carbon monoxide is then oxidized at room temperature with iodine pentoxide yielding carbon dioxide and iodine, either of which may be determined and used as a measure of oxygen content. Unterzaucher (3) adapted the method to the microchemical scale by making various improvements in the apparatus. Modifications permitting the use of larger sample sizes were made by Dinerstein and Klipp (4) in an effort to minimize errors in the analysis of low oxygen content petroleum products. Oita (5) made further modifications in applying the technique to light hydrocarbons. The problems of sensitivity and volatility were overcome by using a magnetically controlled section of spiral quartz tubing as the sample container permitting the use of as much as 5 grams of sample. Although methods based on thermal decomposition require somewhat simpler apparatus and are less subject to interference than the complete oxidation and catalytic hydrogenation methods, time requirements of the order of 60 to 70 minutes per analysis make them equally unattractive for routine use.

The answer to the oxygen analysis problem now appears to be fast neutron activation analysis (6-8). The purpose of this paper is to describe the techniques employed at this laboratory for determining oxygen in petroleum products and related materials by the activation method.

In the determination of oxygen by fast neutron activation, the sample to be analyzed is irradiated with neutrons of sufficient energy to initiate the  $O^{16}(n,p)N^{16}$  reaction ( $Q = -9.62$  Mev). The 7.4-second  $N^{16}$  activity induced in the sample is then measured and the oxygen content computed from the slope of a calibration curve prepared from a series of standards containing known amounts of oxygen. Samples and standards are prepared, irradiated, and counted in exactly the same way; all activities are normalized to a fixed neutron flux and weight.

Fast neutrons for this work are most conveniently produced by bombarding a tritiated target (e.g. tritiated titanium) with deuterons in a relatively low voltage accelerator, the yield of the  $H^3(d,n)He^4$  reaction being such that an adequate output ( $\sim 10^{10}$  neutrons/sec) of 14-Mev neutrons is obtained at accelerating voltages as low as 125 kilovolts.

Either beta-ray or gamma-ray counting techniques can be employed to measure the  $N^{16}$  activity (see Fig. 1). Because of the short half-life of  $N^{16}$ , the irradiation time and the time at which the irradiation stops, as well as the counting time and the time at which the counting starts, need to be very carefully controlled. An automatic timing and sample transfer system is therefore necessary if accurate, reproducible results are to be obtained.

#### INSTRUMENTATION

A diagram of the sample transfer system used for the oxygen analyses with detail sketches of a sample bottle in the irradiation and counting positions is shown in Fig. 2. The system is operated with air at 65 psi and is equipped with three timers and four solenoid valves that automatically time and control the irradiation, transfer, and counting sequence. Samples are transferred through the 32-foot long polyethylene tube, which makes a  $200^\circ$  bend over the top of the shielding wall, in less than 1-1/4 seconds. A photoelectric device is employed at the target end of the transfer tube to assure reproducible positioning of the sample bottles in front of the water-cooled tritiated titanium target (on a 2-mil thick stainless steel backing) of the 130 kilovolt accelerator. The 14-Mev neutron flux on the deuteron beam axis 3/4-inch from the target (center of sample bottle) is approximately  $2 \times 10^8$  neutron/cm<sup>2</sup>-sec with a 250  $\mu$ amp magnetically analyzed ( $20^\circ$  deflection) beam of deuterons ( $D_1^+$ ).

Two 3-inch diameter x 3-inch thick NaI(Tl) scintillation counters are used to detect the 6.1 and 7.1 Mev gamma rays from  $N^{16}$ . The outputs of the two counters are fed in parallel through an amplifier to either a discriminator-scaler or a multichannel analyzer, the latter being needed only to determine the optimum discriminator setting for a given matrix material. (For most petroleum products the discriminator can be set to accept gamma rays with energies greater than about 0.5 Mev without introducing any appreciable error in the oxygen determination.) The neutron output of the accelerator is monitored with a BF<sub>3</sub> counter located in a position in the shielding wall where preliminary tests showed that the total count during an irradiation period would be proportional to the fast flux through the sample. The monitor is used to normalize sample data to a fixed neutron flux thereby compensating for fluctuations due to changing beam and target conditions.

## EXPERIMENTAL

Sample Preparation - The samples, which to date have been predominantly rather volatile liquid petroleum products, are poured into 1/4-ounce polyethylene bottles (weighing about 1.5 grams) fitted with extended dropper tips\* for sealing and machined polyethylene driving caps. Sample bottles are weighed before and after filling and the weight of the sample (~6 grams) determined to 0.01 grams. The filling and sealing operations are carried out in an atmosphere of nitrogen or helium.

Irradiation and Counting - Samples are put in the irradiation position by inserting in a sample loader located near the counter end of the transfer tube and pressing a button which momentarily opens solenoid valves No. 1 and No. 2 (Fig. 2). The irradiation, delay and counting sequence are initiated by a manual switch which simultaneously starts the irradiation timer and the neutron monitor and directs the deuteron beam onto the tritium target by energizing a beam deflector located in the drift tube of the accelerator. After the preset irradiation time (20 seconds), the beam is automatically deflected onto a water-cooled slit stopping the generation of neutrons, valves No. 3 and No. 4 are opened, and the delay timer is started. The delay timer then turns on the counting equipment for a preset counting time (usually 20 seconds) 1-1/4 seconds after being actuated. Experience has shown that the heaviest samples, and consequently the slowest to transfer, reach the counting position within this period. After the counting data are recorded, the cycle is repeated until the desired total count is accumulated.

## DISCUSSION

One of the most important problems to be solved before oxygen analysis by neutron activation can be put on a routine basis is that of obtaining a moderately sized (~5-15 ml), cheap, disposable, sample container. Ideally, the container material should be relatively free of oxygen, fluorine† and other elements that give rise to reaction products with short half lives. Short of this, the concentration of contaminants in the material should not vary significantly from container to container.

Following a rough survey by the fast activation method of the oxygen and fluorine contents of a number of possible container materials, polyethylene was selected for further study. Samples were either machined in the form of solid cylinders (weighing about 6 grams) or cut into small pieces and sealed in a bottle in an atmosphere of helium. They were irradiated and counted as described above. Relative gamma-ray activities per gram measured above a discriminator level corresponding to 0.5 Mev for several types of polyethylene are given in Table I; a polypropylene value is included for comparison purposes.

These results led us to the use of the commercially available 1/4-ounce polyethylene bottle (costing \$37 per thousand) for our standard sample container. Subsequent activation measurements have

\* Tips (No. D13-370) are purchased with the bottles (No. 5-6045) from Erno Products Company, Philadelphia, Pennsylvania.

† N16 is also produced from fluorine by the  $F^{19}(n,\alpha)N^{16}$  reaction.

shown that the polyethylene in these bottles contains approximately 320 ppm of oxygen; changes in oxygen content from bottle to bottle are too small to be detected by present procedures.

TABLE I  
Comparison of Activities Induced in Polyethylene  
and Polypropylene by Fast Neutrons

		Relative Activity Per Gram*
Conventional Polyethylene	Allied Resinous Products, Inc.	2.7 ± 0.4
Linear Polyethylene	Allied Resinous Products, Inc.	1.9 ± 0.2
Marlex 5003	Westlake Plastics Company	1.9 ± 0.2
Polyethylene from Commercial 1/4-Ounce Bottle	Plax Corporation (Erno Products Co.)	1.0 ± 0.2
Polypropylene	Allied Resinous Products, Inc.	5.5 ± 0.6

\* Errors are standard deviations due to counting statistics.

The polyethylene bottle will lose product by diffusion through the wall and become distorted when left filled at room temperature for more than a few minutes with some hydrocarbons, particularly the aromatics. Best results are obtained, therefore, when samples are irradiated and counted immediately after preparation.

Smooth transit of the bottles through the transfer tube is made possible by the lip on the top of the bottle cap (see Fig. 2). Before this feature was added transit times would vary considerably, and occasionally a bottle would be suspended in a vertical section of the tube by the air streaming through the annulus between the bottle and the tube.

## RESULTS

A typical calibration curve for oxygen is shown in Fig. 3 for counts taken above an energy level of 0.5 Mev; the errors are standard deviations from counting statistics. The standards were prepared by mixing known amounts of dibutyl carbitol  $[(C_4H_9OCH_2CH_2)_2O]$  in white mineral oil. After appropriate corrections had been made for variations in neutron flux and bottle weight, the count from a blank run (bottle filled with mineral oil) was used to correct the standard sample counts for the oxygen in the polyethylene and the oil.

Neutron activation results are given in Table II for a group of synthetic samples containing known amounts of added oxygen and a group of typical petroleum product samples. The poor agreement with chemical analysis loses most of its significance when the unreliableness of the chemical method in the range below 1% total oxygen, as exemplified by the data in the third and fourth columns of Table II, is taken into consideration. The two activation analysis values given for the last seven samples are from runs made several days apart using different sample bottles. In all runs, the samples were cycled twice; blank runs were made with helium.

### CONCLUSIONS

The fast neutron activation method for determining oxygen in petroleum products and related materials is accurate and is relatively free of trace element interference in the range above 0.01 per cent. It allows oxygen to be measured faster and with a higher precision than any other method yet developed. With additional developmental work it should be possible to analyze for as little as 10 ppm of oxygen with an error of about  $\pm 20$  per cent.

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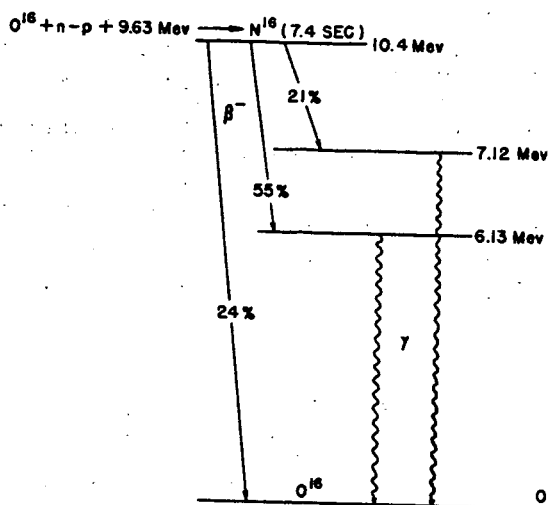


FIGURE 1  
DECAY SCHEME FOR  $N^{16}$

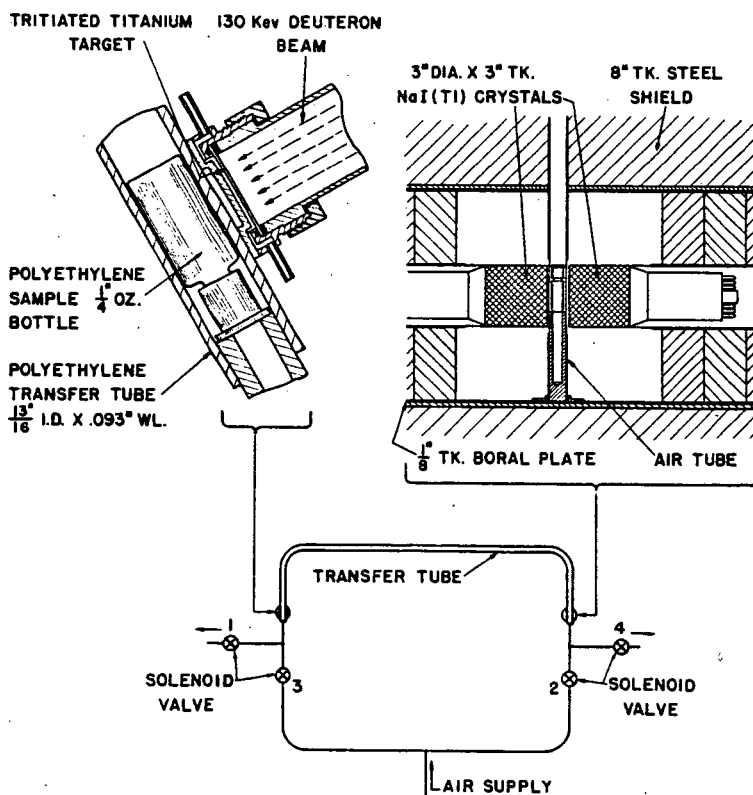


FIGURE 2  
IRRADIATION, TRANSFER AND COUNTING SYSTEM FOR OXYGEN ANALYSIS

TABLE II				
Analysis For Oxygen By Fast Neutron Activation				
Sample	Oxygen Content (%)			
	Calculated	Chemical Analysis		Neutron Activation*
		GR&DC	Commercial Lab	
Mineral Oil	0	---	0.03, 0.12, 0.06	0±0.02
Mineral Oil + Diethyl Carbonate	0.252	---	0.10, 0.11, 0.47	0.24±0.01
Mineral Oil + Diethyl Carbonate	0.556	---	0.31, 0.37, 0.51	0.53±0.01
Mineral Oil + Diethyl Carbonate	1.094	---	0.34, 0.43, 1.08	1.1 ±0.03
GR39362 - Heavy Gas Oil	---	0.30, 0.33	0.20, 0.20	0.22±0.01, 0.21±0.01
GR48962 - Fuel Oil Distillate	---	0.22, 0.24	0.25, 0.20	0.15±0.01, 0.14±0.01
GR53049 - Furnace Oil Distillate	---	0.26, 0.23	0.14, 0.18	0.07±0.01, 0.07±0.01
GR56085 - Light Furnace Oil	---	0.14, 0.12	0.17, 0.22	0.10±0.01, 0.09±0.01
GR58790 - Furnace Oil	---	0.20, 0.19	0.14, 0.18	0.10±0.01, 0.10±0.01
Mineral Oil + Dibutyl Carbitol	0.28	---	0.35, 0.37	0.27±0.01, 0.29±0.01
Mineral Oil + Dibutyl Carbitol	0.73	---	0.67, 0.80	0.73±0.02, 0.72±0.01
* Errors are standard deviations due to counting statistics.				

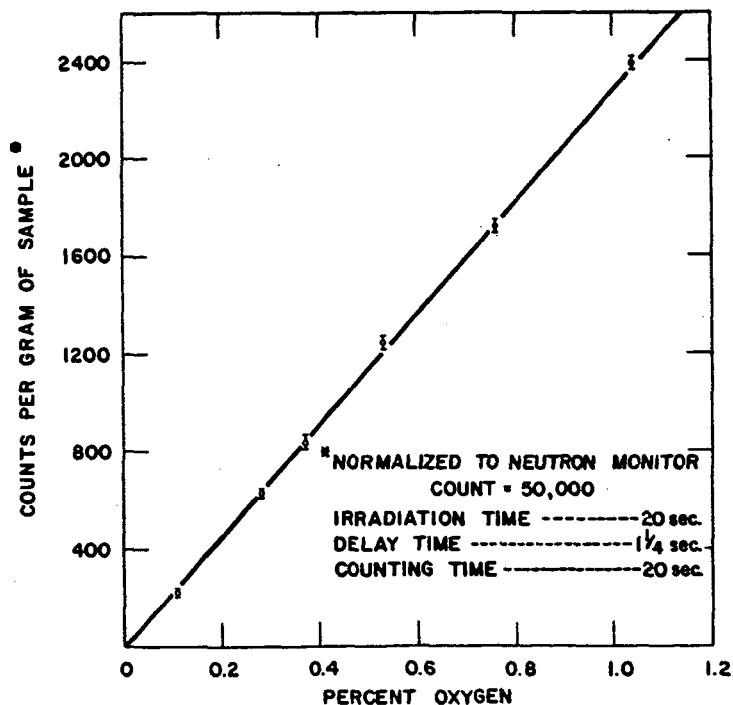


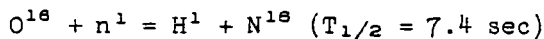
FIGURE 3  
CALIBRATION CURVE FOR OXYGEN

# Activation Analysis of Petroleum Stocks for Nitrogen and Oxygen by Activation with Fast Neutrons

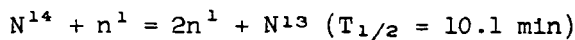
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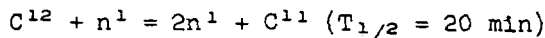
Analysis by radioactivation with neutrons from nuclear reactors is possible for most elements, in some cases with remarkable sensitivity. However, three light elements of particular interest in petroleum refining, carbon, oxygen, and nitrogen, remain quite inert under irradiation with slow neutrons. A number of metallic impurities in petroleum can be determined by activation in a nuclear reactor, but the cost of even the smallest reactor has precluded the routine application of such analyses in petroleum refining and research. In one case, a high-voltage electron accelerator, used primarily for radiation chemistry studies, has been adapted to the part-time production of a moderate neutron flux and used to advantage in routine chemical analysis,<sup>1</sup> but its cost is too great to justify its purchase solely for analysis. The recent availability of low-cost, low-voltage, positive-ion accelerators designed to produce neutrons has brought activation analysis within the reach of the average industrial laboratory. The neutrons formed by 150-keV deuterons impinging on a tritium target have an energy of 14 MeV. This supplies enough energy to activate oxygen by the reaction



and nitrogen by



That the energy is somewhat too small to activate carbon by the similar reaction



is fortunate from the standpoint that hydrocarbons can be analyzed for small concentrations of oxygen and nitrogen (and most of the other elements) without the hindrance of a large interfering carbon activity.

We have installed a Texas Nuclear neutron generator, Model 150-1H, and are using it for analysis of petroleum stocks for various elements by activation with the 14-MeV neutrons. At a beam current of 0.5 milliamperes on a fresh target of titanium tritide on a molybdenum disk, we find a fast neutron flux of  $2 \times 10^{10}$  n/sec. With the sample in a 60-ml bottle adjacent to the



target, we achieve an average flux density in the sample of  $5 \times 10^7$  n/cm<sup>2</sup>-sec. In this paper, we report our experience in nitrogen and oxygen analyses.

### Nitrogen Analysis

A sample up to 60 ml in a polyethylene tube or bottle is exposed to the neutron flux for 10 minutes. Then the bottle is placed in a well in a 3-inch NaI crystal for counting the scintillations produced by the annihilation photons from the N<sup>13</sup> positrons. Alternatively, the irradiated sample is added to a fluorescent mixture for liquid-scintillation counting of the positrons. In either case, one to two minutes is allowed for any oxygen in the sample or container to decay. Then the nitrogen is counted for a period up to 18 minutes. The identity of the radioisotope is confirmed, when necessary, by the half-life of the decaying activity or by the pulse-height spectrum of the annihilation radiation or beta rays. We find with a flux density in a 60-ml sample of  $5 \times 10^7$  n/cm<sup>2</sup>/sec, that a sample containing 1% nitrogen gives an initial counting rate of 1300 counts/sec.

### Flux Monitoring

The variation in beam current and position on the target during a short irradiation or from one irradiation to another, introduces a considerable error into an analysis. The quantity of an induced activity at the end of an irradiation is

$$\int_0^T \left( \frac{dn}{dt} - \lambda n \right) dt$$

where  $\frac{dn}{dt}$ , the rate of production of the radioisotope, is proportional to the neutron flux. If this is constant during the irradiation, the integral has the value  $\frac{1}{\lambda} \frac{dn}{dt} (1 - e^{-\lambda T})$ . However, if the flux is

not constant, using the average value of  $\frac{dn}{dt}$  gives only an

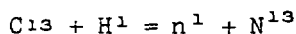
approximation. The final activity may deviate from the above either upward or downward, depending on whether the flux increases or decreases during the irradiation.

We have found a convenient means to monitor the flux and correct automatically for fluctuations during irradiation, as well as for errors in timing. If, during irradiation of a sample, one exposes as a monitor an object in which the neutrons will activate a radioelement of the same half-life as the activity in the sample being analyzed, the monitor will serve to automatically integrate the flux. If both the sample and the monitor are exposed in the same respective geometry in each irradiation, the ratio between the activities in the sample and the monitor will be independent of flux variations, but will vary only in proportion to the element being determined in the sample.

We have used small pieces of copper as suitable monitors for nitrogen. Copper-62, induced by the  $n,2n$  reaction in copper, has a half-life of 9.8 minutes, compared to 10.1 minutes for nitrogen-13. The copper is placed in the same position in each irradiation and then counted for 1 minute, beginning 2 minutes after irradiation, in a small well counter. The count from the nitrogen between 2 and 20 minutes after irradiation is normalized to the copper count. The small difference in half-lives in this case would introduce only a 2% error in normalization if the flux changed by 20% during the irradiations.

### Interferences

At nitrogen concentrations below 0.1%, several substances present in hydrocarbons may produce activities which interfere with nitrogen analysis. Atmospheric nitrogen dissolved in the sample can be as high as 0.03%; it can be purged from the sample before analysis by boiling it or bubbling oxygen through it. Copper has a high cross-section to 14-Mev neutrons for the production of Cu-62. Because it also emits positrons and has a half-life indistinguishable from that of N<sup>13</sup> and because it may occur at low concentrations in petroleum stocks, it can be mistaken for nitrogen. We have been able to separate the two by pulse-height analysis of the spectra in a liquid scintillation counter using the large differences in beta-ray energies. Most important interference, however, is the nitrogen-13 activity produced in hydrocarbons by the protons recoiling from fast-neutron collisions and entering the reaction with carbon:<sup>2</sup>



We have found that this reaction produces as much N<sup>13</sup> as 0.07-0.09% nitrogen in the sample, and this limits the sensitivity for detection of nitrogen in hydrocarbons to about the 0.1% level. Without this inherent interference, the sensitivity would be below 1 part per million.

Even at higher concentrations, the N<sup>13</sup> contribution from this source must be evaluated to give an accurate analysis. Two samples of a lubricating oil additive compound containing 1.83% N according to chemical analysis, as well as a small amount of phosphorus, were diluted by factors of 10.7 and 8.7 in benzene and irradiated. N<sup>13</sup> activities corresponding to 2.56% and 2.48% N were found. The decay of the scintillation pulses between 0.4 and 0.6 Mev fit a 10-minute curve, showing that the concentration of the phosphorus was not enough to introduce a large error. Activation of the benzene alone gave N<sup>13</sup> corresponding to an apparent 680 ppm N. This contribution was subtracted to find the actual nitrogen content of the sample, 1.86%, which agrees with the chemical analysis.

### Oxygen Analysis

Activation analysis has proved particularly valuable for oxygen determination since it is the only method which can give directly the total oxygen in a sample. The analysis is very rapid and subject to few interferences. The nitrogen-16 formed by the  $n,p$

reaction decays with a 7.4-second half-life by emission of beta particles and 6 to 7-Mev gamma rays. Since these gamma rays are twice as energetic as any others encountered in activated petroleum stocks, we can eliminate interferences with a pulse-height selector set to respond only to gamma rays of greater than, say, 4 Mev.

The sample, in a 60-cc polyethylene bottle, is irradiated for 30 seconds, then transferred by pneumatic tube to a 3-inch well scintillation crystal and counted for 15 seconds. The flux monitor consists of a small piece of plastic scintillator, surrounded by lucite and attached to a photomultiplier tube. The scintillator, located a few inches from the target, detects beta particles of  $N^{16}$  produced from oxygen in the lucite. Measurement of this  $N^{16}$  activity normalizes the activity in the sample to the neutron flux used for irradiation of an oxygen standard. Since the sample and monitor are counted simultaneously, the accuracy of analysis does not depend upon precise timing of the start and duration of the counting period. Irradiation and counting of a standard and its monitor plus two or three minutes of calculation completes the analysis.

Samples which have been analyzed by this technique include polymers, lube oil additives, asphalts, and cracker feed stocks. Oxygen contents ranged from 50 ppm to 30%. Duplicate determinations agree to within 2-5%, depending on the level of activity produced. The highest sensitivity is achieved with 50-gram samples, but we have analyzed samples weighing as little as 10 milligrams. For samples containing less than 0.1% oxygen, a correction for oxygen in the polyethylene container becomes significant; and dissolved oxygen in the sample must be removed by bubbling with nitrogen. The only element interfering directly in this analysis is fluorine, which gives  $N^{16}$  via the  $n, \alpha$  reaction. Fluorine is also activated to 29-sec  $O^{19}$ , however; and a measurement of this activity allows correction for the  $N^{16}$  contribution from fluorine.

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New Method of Tritium Labeling of  
Pure Compounds and Coal Derivatives\*

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Introduction

The primary broad objective of this work was to develop the best generalized method of labeling organic materials by exchanging hydrogen with tritium. Of more particular interest was the production of radio-tracers by application of the best tritium labeling method to coal and to products derived from coal by hydrogenation or other processes. These tracers would ultimately be for studies of the mechanism of physical and chemical processes in which these materials are used.

Generally, the materials that are to be labeled for coal processing research are of very complex and usually unknown chemical structure. In such cases, labeling with carbon-14 is precluded since the only method available for incorporating this polyvalent isotope is chemical synthesis. On the other hand, potentially any organic material can be tagged with tritium since the universally present monovalent hydrogen is susceptible to isotopic exchange under proper conditions. This applies to non-descript organic materials as well as pure compounds.

The most important qualification of any labeling method is that it yields tracers of chemical structure identical with the material being labeled. Any production of tagged by-products of altered chemical structure requires stringent post-labeling purification before trustworthy tracers would be obtained.

Two general methods of tritium tagging have been evaluated. The first evaluation was of the more familiar Wilzbach method, which induces self-labeling by the beta radiation from tritium gas in contact with the material to be tagged. Numerous difficulties were found in this method of producing tracers, mostly arising from radiolysis damage to the tracer, as will be pointed out later. Dissatisfaction with the Wilzbach method led to development of a new method, based upon a highly reactive tritiating reagent that promises wide applicability. This latter method utilizes catalytic activity to promote isotopic exchange of tritium into the tracer, as opposed to the radiation induced exchange of the former method with its inherent molecular damage.

Both labeling methods have been tested on hydrocarbons that typify chemical structures expected in coal and coal derivatives, to provide background information for tagging these materials. This is still considered an interim report, in the sense that much more extensive work is indicated to determine the variety of compounds, other than hydrocarbons, that can be

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successfully labeled with the tritiating reagent method. It is conceivable that this method may be sufficiently universal to apply, not only to a wide array of coal and petroleum materials, but also to some pharmaceutical and biological compounds.

Though much work has been done in the past on the use of acids and acid catalysts to promote hydrogen isotopic exchange, especially with deuterium, the past methods have several disadvantages. Some isotopic exchange is obtained with powerful inorganic acids as concentrated sulfuric. However, it cannot be considered as a generalized isotopic exchange reagent because of undesirable sulfonation reactions with aromatic compounds. Also, the exchange rate is often not very fast. Weaker acids as phosphoric require elevated temperatures to effect a reasonable rate of exchange. Under these conditions, undesirable side reactions as formation of tars and polymers are observed for aromatic hydrocarbons.

We then considered boron trifluoride as catalyst to promote isotopic exchange, with tritiated phosphoric acid as the tritium carrier. The boron trifluoride forms a one-to-one molar complex with phosphoric acid and it was soon observed that this complex was a powerful tritiating reagent, free of side product generation for many tested hydrocarbons.

#### Experimental Procedures

##### General

Three methods of assay of the specific activity of tritium in tagged samples were examined. The zinc fusion - gas ion chamber method was tried initially. The method has been described in detail by Wilzbach<sup>1,2</sup> and by Tolbert<sup>3</sup>. The total sample is gasified to a mixture of mostly H<sub>2</sub> and CH<sub>4</sub> and the radioactivity of the gasified material determined in a gas ion chamber as described by Tolbert<sup>3</sup>. The ion current is measured with an electrometer. This method was satisfactory for materials of high activity, of 100 uc/gm or more. It did not have sufficient sensitivity for accurate assay of low activities such as 1 to 0.1 uc/gm because of extraneous fluctuating background readings.

The second method tried was direct liquid scintillation counting of the sample. A single channel counting apparatus was assembled as described by Hodgson and Gordon<sup>4</sup>. A special low, dark current, low noise photo multiplier tube (Type 9536A, EMI Electronics Ltd., England) was used in a cold box at -10°C for sensing the scintillations. Attached electronic counting apparatus consisted of a preamplifier and commercial scaler. The method was satisfactory for relatively few pure colorless liquids. Many of our materials, either natural or model compounds, are colored or highly quenching in the liquid scintillators and cannot be counted this way.

The final method adopted is applicable to all types of organic products, including highly colored natural materials. The method is one that has been previously recommended by Quinn<sup>5</sup> and involves dry combustion of the sample followed by liquid scintillation counting of the collected product water by well-established water-counting techniques. The method is more rapid than zinc fusion, up to 20 samples per day can be assayed as opposed to about 4 for the former method. It is sufficiently sensitive for accurate assay of specific

activities down to 0.01  $\mu\text{C/gm}$ . Sensitivity could probably be extended another order of magnitude by use of more modern dual channel liquid scintillation counters.

To test for radio-chemical purity of tracers, or conversely, the distribution of tritium among impurities and parent tracer, vapor phase chromatography was used in the manner described by Riesz and Wilzbach<sup>6</sup>. A sample is elutriated through a Perkin-Elmer chromatograph. The effluent from the chromatograph was passed through a thermal conductivity cell and a continuous flow ion chamber in series. A dual chromatograph was thus obtained. The recorded output of the thermal conductivity cell shows the mass associated with each elutriated peak while the recording of the ion chamber current gives the amount of radioactivity associated with corresponding peaks. In some cases, tagged tracers are of low activities, below the sensitivity of the ion-chamber detector. In these cases, the elutriating peaks are collected individually in ice traps and then assayed by combustion and liquid scintillation counting.

#### Wilzbach Method

The Wilzbach<sup>1,2,6,7,8</sup> method of labeling has been well described in previous literature. It consists of exposing the material to be tagged to several curies of pure tritium gas in a sealed reaction vessel for several days. Tritium exchange for bound hydrogen occurs under the influence of the beta radiation from the tritium. Unfortunately, besides isotopic exchange, the parent compound undergoes radiolysis such that highly tagged side products are always produced. Thus, it becomes important to determine the distribution of the tritium between the parent unmodified compound and that of the side products of altered chemical structure. This was done according to the chromatography procedure described above. Purification of labeled materials produced by this method was carried out by preparative vapor chromatography as well as ordinary techniques as micro-distillation and crystallization.

#### $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$ Method

The procedure for making and using the phosphoric acid-boron fluoride tritiating reagent is very simple as indicated in Figure 1. First, tritiated water and phosphorus pentoxide are mixed stoichiometrically to give absolute tritiated phosphoric acid. Then boron fluoride gas is bubbled into the acid until it is saturated (absorption is rapid) which yields a one-to-one ratio of  $\text{BF}_3$  to acid, forming the complex shown in Figure 1. This complex reagent is a very dense liquid, immiscible with all hydrocarbons, but soluble in organic compounds containing oxygen. This reagent must never be stored in glassware for extended times. An imperfect seal, allowing long water vapor absorption will lead to hydrofluoric acid attack of the glass sufficiently to dissolve through the container. Polyethylene ware is used for long-term storage as well as for tagging experiments that extend beyond 2 or 3 days. Ordinary glassware can be used with the reagent in experiments lasting a day or two.

The specific activity of tritium in the water used to form the reagent is the primary determinant of the specific activity of the ultimate tracer treated with the reagent. Thus if very high specific activity tracers are desired, high concentrations of tritium oxide are used in making the phosphoric acids.

To tag an organic liquid, it is simply stirred in a round-bottom flask with the reagent. Solids are ground fine and slurried with the reagent. The ratio of reagent to material being tagged is arbitrary, determined by whether one wants to transfer most of the tritium in the reagent to the material or only a little. At equilibrium, the tritium atoms in the mixture are statistically distributed among all exchangeable hydrogen positions, including the three of phosphoric acid. In this preliminary work, we have used a 2 to 1 mass ratio of material being tagged to reagent.

In tagging of coal and coal extract, the material was first ground to -200 mesh before contacting the reagent. The tagged solids were recovered by filtration. The cake was washed three times with water and twice with 1% NaOH solution and again with water until neutral.

After exchange tagging, hydrocarbon liquids as toluene are simply recovered by decantation in a separatory funnel and solids are collected by filtration. If the organic material dissolves in the reagent, as anisole does, then a few drops of water carefully added to the mixture will result in separation of the organic phase for decanting. The tracer is then washed several times with water and dilute sodium bicarbonate to remove all of the reagent and labile tritium.

The radio-chemical purity of the tracers produced with the  $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$  reagent is demonstrated by examining for any loss in specific activity when the tracers are subjected to three stages of purification. The product is first treated with sodium to eliminate any labile tritium. This is followed by fractional distillation and finally by preparative chromatography with discriminative collection of the single peak identified as the original compound. We have found that these purity tests are more dependable than the dual radiation-mass detection chromatography alone.

Solid materials such as coal extract and coal were only tested for gross physical changes after tagging, such as melting point.

### Results

#### Evaluation of the Wilzbach Tagging Method

A series of pure aromatic hydrocarbons, typical of hydrocarbon types found in coal hydrogenation oils, were tagged by the Wilzbach method. The results obtained are given in Table I. Included are the tests for radio-chemical purity of the labeled products as determined only by vapor phase chromatography with dual radiation and mass detectors. It is noted that the apparent radiolysis damage decreases both with increasing aromaticity and with the number of fused rings. In general, the amount of radiolysis damage seemed encouragingly small for high molecular weights. The method was then likewise applied to the tagging of a series of narrow-boiling fractions of oils derived from coal hydrogenation. Boiling points ranged from 233 to 355°C and the oils are considered as high molecular weight. Here again, the apparent amount of radiolysis damage was quite small. With the exception of one of the middle boiling fractions, the percent tritium in side products seen on the dual chromatographs was five percent or less.

However, such anomalous results were obtained in experiments with the Wilzbach tracers, even with the simple compounds purified by chromatography, that more rigorous examination of radio-chemical purity became imperative.

Naphthalene was chosen for a more stringent investigation of the purity of the Wilzbach tagged material. The naphthalene newly tagged for this investigation appeared, by chromatography, to have even less tagged impurities, i.e., 6.3 percent as opposed to 13.1 percent for the earlier sample shown in Table I. Suspecting hold-up of some radiolysis impurities in the chromatograph, the tritiated naphthalene was run through a fresh column which was then flushed with water vapor. This revealed that only 62% of the radioactivity elutriated with the naphthalene peak, 4% with the light hydrocarbon impurities and 34% was flushed out by the subsequent water. Therefore at least 34% of the tritium was in unstable radiolysis products that were retained by the column. Thus, at best the naphthalene could be only 62% radio-chemically pure. This points out that one should not view radio-chromatography as a sufficient test of radio-chemical purity.

Next, diluted, tritiated naphthalene was run through a series of purifications as shown in Table II. The sodium treatment was suggested by the possibility of labile tritium in radiolysis impurities, that could have transferred to the chromatographic packing (Perkin-Elmer Type A) and then be flushed out by water. Since there is no labile hydrogen in naphthalene, the observed drop in specific activity upon sodium treatment is due to such hydrogen in radiolysis impurities. Recrystallizations slowly but definitely decreased specific activity - further evidence of radio-chemical impurity. Fraction distillation (under vacuum) reduced drastically the specific activity of the center cut of naphthalene, down to about a third of the initial activity. Thus distillation reduced the specific activity more than chromatography, showing that all that elutriates with the naphthalene peak from the chromatograph is not tagged naphthalene. The longer residence time at elevated temperatures in distillation may have removed unstable radiolysis products, such as by polymerization, making distillation a more efficient purifier than chromatography. The question mark in the last row of Table II indicates that even after the shown purification schemes, there is not absolute assurance that the naphthalene is completely radio-chemically pure. In fact, using this final tagged naphthalene in a de-tagging isotopic exchange test with benzene at 380°C resulted in 16.6% loss of tritium from the naphthalene, whereas when tritiated naphthalene produced chemically (and more likely pure) was used under the same conditions, no exchange loss of tritium was observed.

Thus, radiolysis during self-labeling, produces contaminants, in trace chemical amounts but of very high specific activity, which have physical properties so closely resembling the parent compound or so minute in quantity, that they are not distinguished by chromatography and defy all but the most painstaking purifications which may be prohibitively extensive. It follows that but little specific activity remains in the purified tracer.

We are not alone in these observations of purification problems with the Wilzbach method, as several others reported in late 1960 or early 1961. To cite a few others, a group working at the University of Rome<sup>7</sup> on self-labeling of substituted benzenes and a Bureau of Mines Group<sup>8</sup> that labeled numerous organics associated with gasoline, had both then observed that careful purification is required. Wilzbach<sup>9</sup> too has pointed this out - quote<sup>9</sup> "In view of the number of tritiated impurities which are likely to be present, it is perhaps remarkable that radio-chemical purity can be achieved for any but the simplest of compounds", unquote.



At this point, it was deemed wise to search for another method of tritium labeling, for certainly if simple single compounds are so difficult to obtain radio-chemically pure, it would be practically impossible to completely remove radiolysis contaminants from complex mixtures derived from coal.

#### Evaluation of the $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$ Tagging Method

Initial work was carried out on the evaluation of concentrated sulfuric acid as a reagent for isotopic exchange tagging of tetralin. This method was abandoned when it was found that the formation of sulfonation products could not be avoided and tagging was rather slow. Phosphoric acid was next tried as a reagent. Elevated temperatures of  $85^\circ\text{C}$  or higher were required to obtain reasonable tagging rates. At these temperatures, by-product materials were formed by apparent polymerization reactions, invalidating this approach.

All subsequent work was devoted to the use of the tritiated phosphoric acid - boron fluoride complex as the tagging reagent. It was soon found that this material was a very powerful tritiating reagent which overcomes the deficiencies outlined above for other acids, i.e., it is both non-destructive and fast.

Some initial results of tagging with the tritiating reagent are shown in Table III. These compounds were all mixed with half their weight of  $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$  which had a specific activity of  $1400 \text{ uc/gm}$ , except for anisole where the reagent had a specific activity of  $380 \text{ uc/gm}$ . The degree of tagging shown was accomplished in less than 8 hours. It is immediately apparent that the aromatic compounds tag very rapidly as demonstrated by the first five listed in Table III. The non-aromatics that contain a hydrogen on tertiary carbon, namely methylcyclohexane and decalin also tag but at a lesser degree. The non-branched aliphatics as exemplified by cyclohexane and n-octane appear not to tag at all. In fact, fractional distillation and preparative chromatography practically eliminates the tritium activity from these two purified aliphatics. Thus there seems to be some selectivity in this method of labeling, with preferential labeling of aromatic hydrogen positions, considerably less for hydrogen on tertiary carbon atoms and essentially none for non-tertiary alkane hydrogen. Future studies will determine the degree of labeling of other forms of hydrogen as those on carbon atoms adjacent to carbonyl groups and other chemically activated forms.

The radio-chemical purity of the tracers produced with  $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$  is demonstrated by comparison of the last two columns in Table III and is indeed encouraging. The three purification steps applied were described earlier. The purity results, that is the agreement between the last two columns in Table III, indicate that essentially all the tritium radioactivity is in the radio-chemically pure tracer, recoverable at yields better than 90%. The small tagging observed in the last two compounds - the non-branched aliphatics - is attributable to chemical impurities originally present before tagging. Indications are that in most cases, if one starts with an absolutely pure compound, after-purification of the tracer is unnecessary and the only reaction that occurs is tagging by exchange of tritium for hydrogen. This was most gratifying as opposed to finding the major portion of bound tritium in radiolysis impurities in the Wilzbach method. In compounds studied so far, only isooctane exhibited some formation (about 0.5%) of new side products upon treatment with the tagging reagent. These side products are easily distinguished and removable by preparative chromatography.

It is interesting to note in Table III that *cis* and *trans* decalin do not tag at identical rates. Also note that naphthalene was tagged in cyclohexane solution (10%) to facilitate contact with the reagent.

Some preliminary kinetic data on tagging with the  $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$  are presented in Figures 2 to 5. Figure 2 compares the tagging rates of three aromatic compounds under similar conditions. Tetralin and toluene tag much more rapidly than benzene. This is due to the molecular electronic directional influence of the substituted groups on the benzene ring which activates aromatic hydrogen exchange.

It is seen from Figure 4 that anisole tags even more rapidly than tetralin or toluene. This is in line with the expected stronger electronic directional influence of the ether substituted benzene ring than the methyl substituted ring.

Figure 3 clearly illustrates the strong temperature dependence of tagging rate as observed for benzene. Thus tagging to equilibrium can be accelerated in cases which may be relatively slow.

Attention was then turned to tagging solids, including coal and derived products. Some results are shown in Figure 6. The coal extract, derived by hot tetralin extraction of a Pittsburgh Seam coal (Ireland Mine) is solid at the tagging temperature of 23°C. The amount of tritium exchange to the extract is obviously quite low, which is at least partly due to the fact that it must be predominantly a surface reaction. The coal itself (Ireland Mine) as shown in Figure 6, tags at an even slower rate than the extract. The reason for the lower rate is not clear though it may be a reflection of more isotopic or molecular diffusion in the extract.

Another sample of Pittsburgh Seam coal, but from the Montour No. 4 mine, was used to study the tagging rate over an extended period of time, i.e., 120 hours. These results are in Figure 7. A fresh sample of coal was used to reduce effects of oxidation. The coal also had been extracted with boiling methanol to remove any resinous materials from the coal particle surface that might inhibit contact with the labeling reagent. The results show that the coal continues to be exchange-labeled over a long period, probably by tritium diffusion through the solid coal. The theoretical limit (explained later) of labeling all of the 4.53% hydrogen content of this coal is 585 uc/gm as compared to only 30 uc/gm attained in 120 hours.

Solid naphthalene was tagged in the same way as coal with the results also shown in Figure 6. It tags even more slowly than coal. However, when naphthalene is tagged in the form of a 10% solution in cyclohexane, the tritium exchange is very rapid as is seen in Figure 6. It is apparent that the slow rate of tagging of coal and extract is primarily due to slow tritium diffusion through the solid and not necessarily connected with any deficiency of exchangeable aromatic hydrogen, since the aromatic naphthalene also tags very slowly in the solid state.

### Discussion

#### Products of Wilzbach Tagging

It is clear that the chromatograph is not a sufficient criterion for radio-chemical purity of tracers produced by the Wilzbach method from polycyclic

hydrocarbons. The results indicate that many of the tagged products, from naphthalene, for example, are unstable tritium addition products rather than the desired isotopic exchange products. Some of these, as ditritio derivatives, may be unseparable chromatographically from naphthalene. Both the labile character of the tritium as seen by their ease of removal with sodium and the suggested polymerization in the chromatograph (hold-up), would fit the properties of compounds of this type.

It may be concluded that the Wilzbach tagging method is unsuitable for the production of reliable tracers from polycyclic aromatic compounds. Required post-tagging purification is too extensive.

#### Equilibrium Tagging With the $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$ Reagent

A postulated mechanism of exchange labeling of an aromatic with the reagent was illustrated in Figure 1. It is likely that the powerful acidic properties of the complex cause formation of carbonium ions, accompanied by a proportional probability of adding a tritium ion to the organic compound. This meta-stable ion can then lose a hydrogen ion, yielding the tritium tagged compound.

The calculation of the theoretical limit of tagging is based on the assumption that at equilibrium the tritium is statistically distributed between all exchangeable hydrogen positions in the compound being tagged and in the phosphoric acid complex. This leads to the following expression for the tracer specific activity ( $S_x^\infty$ ) obtained at equilibrium, or ultimate labeling, as a function of initial specific activity of the reagent ( $S_r^\circ$ ), the weight ratio of tracer to reagent ( $w_x/w_r$ ) and the number of exchangeable hydrogen positions ( $N_H$ ) in the tracer.

$$S_x^\infty = \frac{S_r^\circ}{\frac{3}{166} \frac{M_x}{N_H} + \frac{w_x}{w_r}} \quad (1)$$

$M_x$  is the molecular weight of the tracer compound.

As seen in Figure 3, the experimental limit of tagging of benzene at 65°F coincides well with the theoretical limit calculated from Equation (1), where  $w_x/w_r = 0.5$  and taking  $N_H = 6$ . Though not given in this figure, long-term tagging studies of benzene have shown that the same equilibrium specific activity is reached in 80 hours at 23°C.

In Figure 5, it is seen that tagging of toluene at 23°C is approaching the calculated limit of tagging for five hydrogen positions but not for eight, i.e., all the aromatic positions are being tagged but not those on the methyl group. If tagging were being restricted to only the ortho and para aromatic hydrogens, then the limit would be that calculated for 3 hydrogens. Since this is exceeded by the experimental curve, the meta hydrogens must also be tagging, but likely at a lower rate than the ortho and para types.

Similarly, in Figure 2, the results with tetralin show the experimental limit to agree with the calculated limit for four exchangeable hydrogen positions which again corresponds to tagging of all of the aromatic positions only.

Anisole tagging, as shown in Figure 4, again behaves like that of toluene. The comparison of experimental limit of tagging with those calculated for 5 or 8 exchangeable hydrogens again indicates that only the 5 aromatic hydrogen positions are labeled and not the 3 on the methyl group.

Firmer conclusions can be reached from equilibrium tagging relative to the number of exchangeable positions by using a large excess of tritiating reagent. This improves the resolution between levels of tagging when different numbers of exchangeable hydrogen are considered. If  $w_T \gg w_X$ , then equation (1) reduces to the expression

$$S_X^\infty = S_T^\infty \left( \frac{166}{3} \right) \frac{N_H}{M_X}$$

and the equilibrium specific activity is thus proportional to the number of exchangeable hydrogens. On the other hand if  $w_T \ll w_X$ , then the specific activity of the compound becomes independent of  $N_H$ . Future work will therefore be carried out to confirm the number of exchangeable positions by the use of a large excess of tritiating reagent.

For the weight ratio used in this preliminary work,  $w_X/w_T = 0.5$ , the equilibrium tagging limit is not very sensitive to the number of exchangeable hydrogen positions. The relative values for  $S_X^\infty$  for toluene for 3, 5 and 8 exchangeable positions with the above weight ratio are 1:1.1:1.15, whereas using an excess of reagent would spread the relative values of  $S_X^\infty$  to 1:1.67:2.67.

#### Preliminary Examination of Exchange Reaction Kinetics

The kinetics of the isotopic exchange reaction with the tritiating reagent may be discussed using the mechanism shown in Figure 1 as a basis. It may be assumed that the opposing reaction rates are first order with respect to the concentration of the exchangeable hydrogen positions in the tracer and to the concentration of tritium in the tritiating reagent. Since we are often dealing with a two-phase system, absolute rate constants cannot be obtained. This is true since the rate is undoubtedly a function of the amount of interfacial contact area between the hydrocarbon and the phosphoric acid phases. Meaningful comparative rate data can be obtained, however, if constant conditions of agitation and a constant ratio  $w_X/w_T$  is employed in a series of comparable experiments.

It is known from prior work on deuterium exchange that aromatic hydrogens in different positions relative to orienting substituents on the benzene ring undergo exchange at considerably different rates. The rate equation for aromatic exchange can therefore be written in generalized form as

$$\frac{dS_X}{dt} = \sum_i k_i \left[ S_T \left( \frac{N_{H_i}}{M_X} \right) - S_{X_i} \left( \frac{N_{H_T}}{M_T} \right) \right] \quad (2)$$

Subscript  $i$  denotes the various types of exchangeable hydrogen and  $S$  denotes specific activity. The second term on the right side of the equation corresponds

to the retardation effect of the reverse process, i.e., exchange of tritium from the compound with hydrogen in the reagent. It is assumed that the ratio of tritium to hydrogen is equal in both the reagent and compound after equilibrium is established and thus the rate constants of the forward and back reaction are equal.

The integration of equation (2) becomes rather complex when the specific activity of the reagent decreases during the course of the reaction. The initial rate can be used if desired to obtain a "weighted" average rate for all the exchangeable hydrogens

$$\frac{dS_x}{dt} = S_r \sum_i k_i \left( \frac{N_{H_i}}{M_x} \right) \quad (3)$$

However, due to the wide variation in rates between different exchangeable hydrogens the calculation of such an average rate would have little significance.

It is necessary to use the integrated form of equation (2) to derive values for the individual rate constants. To facilitate such integration, future kinetic data will be obtained under conditions where a large excess of reagent is employed, i.e., where  $S_r$  may be treated as constant. Integration of equation (2) becomes rather simple under such circumstances and leads to the expression

$$S_x = \frac{S_r M_r}{N_{H_r}} \sum_i \frac{N_{H_i}}{M_x} \left( 1 - e^{-k_i \frac{N_{H_r}}{M_r} t} \right) \quad (4)$$

Though no data were yet taken with such an excess of reagent, sufficiently extensive data were obtained on benzene to permit calculation of rate constants in this particular case without having  $S_r$  constant. Since benzene has only one type of hydrogen, integration of equation (2) is rather simple in spite of the fact that  $S_r$  varies with time under the conditions of our experiments. The result is

$$\ln \left( \frac{1}{1 - S_x/S_x^\infty} \right) = k \left( \frac{N_H}{M_x} \right) \left( \frac{S_r}{S_x^\infty} \right) t \quad (5)$$

To derive values of the rate constants one merely has to plot the logarithmic term on the left versus time. This has been done for the benzene rate data at various temperatures and the results are given in Figure 8. The best straight lines were drawn through the data by the method of least squares. The fit to straight lines is rather good as seen. For example, the statistically

calculated correlation coefficients for the data at 21 and 45°C are 0.969 and 0.993 respectively. The values of the rate constants,  $k$ , are

$k (hr^{-1})$	$t (°C)$
0.16	21
2.19	45
7.93	65

The apparent activation energy, calculated from an Arrhenius plot of only three points of rate constant versus temperature, cannot claim much accuracy but yields a value of about 17,700 cal/mol.

A comparison may be made with recent rate data by Olssen<sup>10</sup> on the rate of isotopic exchange between benzene and tritiated 80%  $H_2SO_4$  acid at 25°C. The rate constant for the  $BF_3$  reagent is greater by a factor of 200. The rate constants in heterogeneous systems of this type are, of course, not strictly comparable. Yet, the comparison shows, at least qualitatively, the very powerful nature of the  $TH_2PO_4 \cdot BF_3$  reagent for promoting isotopic exchange.

#### Advantages of the $TH_2PO_4 \cdot BF_3$ Labeling Method

Many advantages of this new method of labeling with the tritiating reagent,  $TH_2PO_4 \cdot BF_3$ , have been demonstrated, as compared to the radiation induced self-labeling method. A summary of these follows:

1. Virtually radio-chemically pure tracers, without highly tagged side products, are produced in many cases. This obviates the extensive after-purification required in the radiation method. One has more faith in the tracer produced.
2. It is more rapid. The desired labeling can often be accomplished in a few hours as compared to several days by the latter method.
3. It is less involved. Ordinary chemical laboratory ware will suffice instead of special vacuum trains and gas handling systems.
4. It is less hazardous from a radiological health standpoint, because it avoids using multicurie amounts of radioactive gas (tritium) with the inherent possibilities of leakage in gas handling systems.
5. High specific activity tracers can be produced when desired. Tracer activity is easily controlled by the amount of tritium one chooses to incorporate in the reagent and the ratio of reagent to tracer compound mixed for labeling. The tagging reagent is very simple to manufacture from inexpensive tritiated water. It is a non-volatile liquid and need not incorporate much more tritium than wanted in the final tracer. Tracer specific activities of over a curie per gram can be produced when desired for experimental studies that will result in high dilution.

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Table I

Results of Tritium Tagging by Wilzbach Method For Model Compounds  
According to Dual Radiation - Mass Chromatography

Material	Tritium Activity In Irradiation (Curies)	Irradiation (Curie-Hrs)	Specific Activity		Percent in Radiolysis Impurities
			Non- Purified Product	In Parent Compound	
Decalin	10	2620	387	204	47.2
Tetralin	8.1	2100	242	155	35.8
Naphthalene	9.4	2680	745	647	13.1
Phenanthrene	5.9	2420	79.9	79.9	0.2
Dihydrophenanthrene (60%)	6.1	1317	118	112	5



Table II

Naphthalene Tritiated by Willzbach Method

<u>Purification Treatment</u>	<u>Resultant Specific Activity (uc/gm)</u>
None	80.0
Na Treatment of Benzene Solution	56.0
Recrystallization From Benzene	53.9
Recrystallization From Methanol	50.4
Fractional Distillation	26.0
Complete Purification	?

Table III

Tritium Tracers Produced With  $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$  at  $23^\circ\text{C}$ 

<u>Labeled Compound</u>	<u>Reaction Time (Hrs)</u>	<u>Specific Activity Before Purification (<math>\mu\text{c}/\text{gm}</math>)</u>	<u>Specific Activity, Purified Tracer (<math>\mu\text{c}/\text{gm}</math>)</u>
Benzene	6.0	106.6	108.2
Toluene	6.5	550.0	554.0
Tetralin	5.5	536.0	531.0
Naphthalene	7.0	1422.0	1440.0
Anisole	6.0	146.0	146.0
Methylcyclohexane	6.0	9.25	9.36
Decalin	6.0	32.2	31.4
cis - Decalin	6.0	-	52.5
trans - Decalin	6.0	-	23.8
Cyclohexane (99.6%)	6.0	0.96	0
n-Octane (98.6%)	6.0	16.3	0

Figure 1

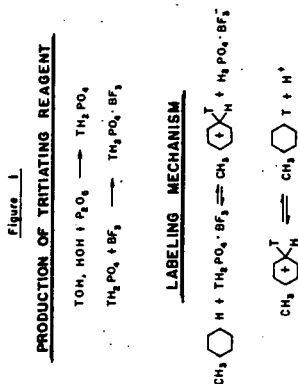


Figure 2

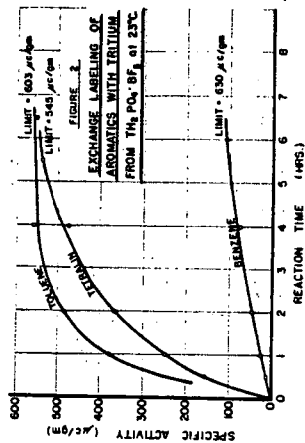


Figure 3

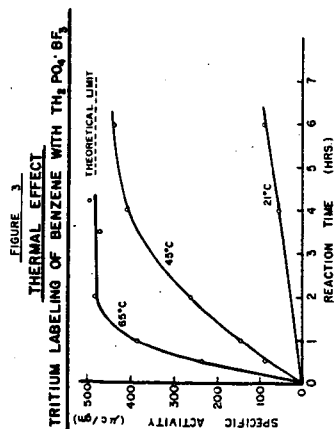


Figure 4

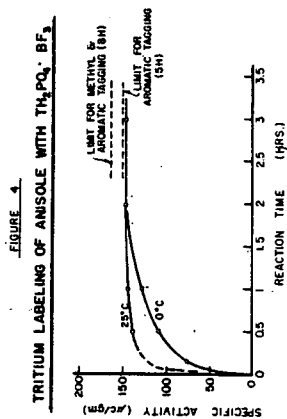


Figure 5

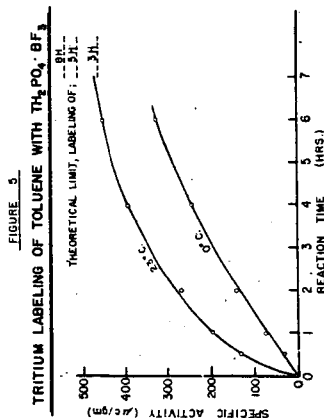


Figure 7

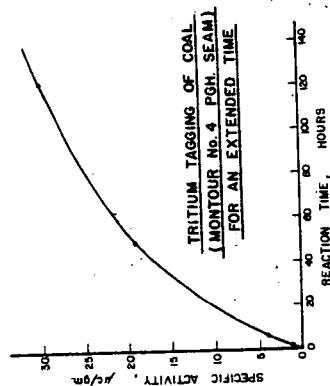


Figure 6

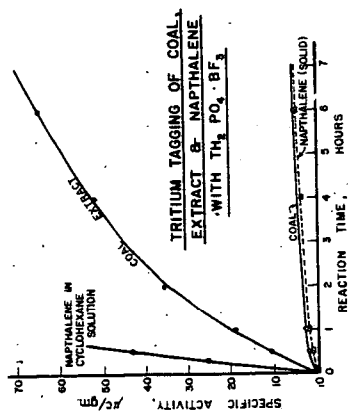
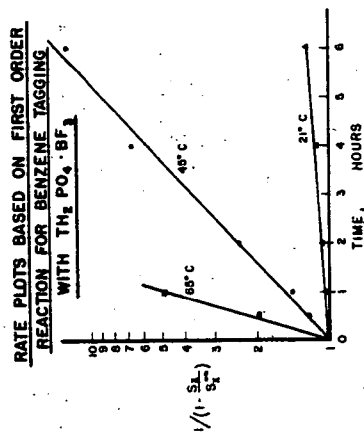


Figure 8



Gamma Ray Viscometer-Densitometer for  
Oils at High Temperature and Pressure

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Introduction

The manufacture or reprocessing of liquid hydrocarbons derived from either coal or petroleum often involves high temperatures and pressures, notably in hydrogenation or reforming units. The accurate design of such units, particularly the liquid handling systems, thus depends heavily upon knowledge of the physical properties of the liquid inventories or oils at the rigorous conditions employed in the units. Viscosity and density data for liquids at very high temperatures and pressures are indeed sparse in the literature, for even the more familiar liquids. Such engineering data are almost certain to be completely unavailable for new products and processes so that the necessary data must be obtained directly on the new materials.

The instrument described here was developed, in particular, to measure the viscosity and density of coal oils at temperatures up to 450°C and pressure up to 5000 psig, conditions used for further hydrogenation. However, the instrument is of widespread interest since it can be used to gain data on any liquid under extreme conditions.

Gamma radiation is perhaps uniquely applicable to determine liquid properties under such drastic conditions. The necessary heavy equipment to maintain these conditions precludes the use of more conventional measuring techniques.

Experimental Equipment

A schematic diagram of the apparatus is given in Figure 1. The arrangement shown is that for viscosity measurements. The liquid is contained in a controlled temperature autoclave that can be maintained under high pressure. Basically, viscosity is determined by measuring the falling velocity of a plummet in the liquid. The special shape of the plummet facilitates measurement of the velocity. It consists of two wide disc ends connected by a thin stem. The gamma ray beam traverses the column of liquid. As the plummet falls through the gamma ray beam, the two heavy ends absorb much of the beam and the stem absorbs but little. Continuously recorded observation of the beam intensity yields two deflections and from their time separation and the size of the plummet, the velocity is easily calculated.

The clearance between plummet and inner wall of the vessel is small, of the order of 5 to 10 thousandths of an inch. This is to suit the low viscosities at high temperatures, i.e., to give a falling velocity slow enough to be accurately

measurable. For such close clearance, a very finely machined sleeve must be used as the inner wall to eliminate wall irregularities of the autoclave. Sleeve and plummet are of the same stainless steel (type 304) to avoid thermal expansion differences.

The gamma ray source is a 5 millicurie sealed source of cesium-137, encased in a 4-inch lead cylinder. A quarter-inch hole drilled through to the source serves as the collimated aperture for the gamma ray beam. Because of sensitivity, a scintillation counter is preferred for detecting the beam intensity and its output is measured by a count-rate-meter (Nuclear-Chicago Corp., Model DS-101 and Model 1620BS respectively). The count rate is continuously recorded on a 1 milliamp strip chart recorder (Esterline-Angus Model No. A. W.) to accurately obtain the time increment for the passage of the ends of the plummet.

The heater encased autoclave is mounted on a pivot. It can thus be inverted to allow the plummet to fall back and forth for repeated collection of velocity data.

Density is measured with the same unit, except that the autoclave is turned 90° into a horizontal position. The source, detector and gamma ray beam are thus lined-up axially with the liquid column. Liquid density is measured by gamma ray absorption. Doing so through the length of the column optimizes the sensitivity of the measured absorption to liquid density.

For the density measurements, the count-rate-meter and recorder are replaced by a gamma radiation analyzer and scaler (Nuclear-Chicago Corp. Model No. 1810 and Model No. 181 respectively). Radiation pulses or counts from the scintillation counter are discriminated by the analyzer which is set to select only those counts due to the primary 0.66 mev gamma rays from the cesium-137. This eliminates background scattered radiation from the counting. Otherwise, the count rate due to scatter so overwhelms small differences in primary ray absorption that small differences in liquid density cannot be discerned accurately. Discrimination thus enhances the accuracy of the method for measuring density by at least an order of magnitude. Discrimination is, of course, not possible with the less expensive Geiger Tube counters, making the scintillation counter necessary here.

#### Calibration

Empirical calibrations are used for both the viscosity and density measurements.

Some typical responses obtained on the counting recorder when calibrating the viscometer are shown in Figure 2. Note the well-marked deflections when the bottom and top of the plummet pass through the gamma ray beam. Measurement of time between deflections is quite accurate, to three significant figures. From these primary data, an empirical calibration of viscosity against observed falling time (velocity can be used if one chooses) is obtained as shown in Figure 3. An excellent straight line relationship is obtained on a logarithmic plot, confirming that terminal velocity of the plummet is being observed in the viscometer. This is predicted by fundamental viscosity relationships for terminal velocities of falling bodies. The five points plotted in this calibration were obtained by using trichloroethane, benzene, water and two NBS standard viscosity oils at 25°C. Similarly calibrating two more plummets with larger clearances yields a useful measurement range of 0.4 to 20,000 cp for this viscometer.

Both in the calibrations and measurements with the viscometer, the bouyancy effects on the plummet by liquids of different densities are corrected for by

$$\Delta T = \Delta T_0 \left( \frac{\rho_0 - \rho_x}{\rho_0 - 1.00} \right)$$

where

$\Delta T$  = corrected falling time

$\Delta T_0$  = observed falling time

$\rho_0$  = density of steel (plummet)

$\rho_x$  = density of liquid studied.

This equation refers all bouyancies to that of water at a density of 1.00, an arbitrarily chosen reference. Any other would serve as well. The equation derives from the first order approximation that the falling time is proportion to bouyancy. If the density of the liquid in the viscometer is not much different than 1, then the correction is negligible.

As a densitometer, the apparatus was empirically calibrated by alternatively filling it with materials of known density, namely, air, benzene, water, trichloroethane and carbon tetrachloride and observing the gamma ray transmission. The transmission,  $T$ , is arbitrarily defined as  $T = C/C_0$  where  $C$  is the counts per minute observed for the discriminated gamma beam after passing through the filled autoclave and  $C_0$  is the count rate obtained from a small reference radiation source attached to the scintillation counter in fixed geometry that can always be duplicated.  $T$  is thus put on a common basis which eliminates effects of instrumental sensitivity drifts during an extended study. As expected, an almost straight line relationship is obtained for the logarithm of transmission versus density as shown in Figure 4. Perfect linearity is not expected because of absorption in the autoclave walls and heater. The plummet may remain during densitometer calibration and use.

### Results

Some exemplary data are given in Figure 5, on the temperature dependence of viscosity of high molecular weight oils obtained by partial hydrogenation of coal. The plots approximate the rough empirical law for liquid viscosity dependence on temperature, i.e.,  $\log \eta = \frac{A}{T} + B$ , where

$A$  and  $B$  are constants. Strict linearity isn't expected for mixtures of compounds as here studied. These results serve here only to illustrate the type of data that can be obtained with this viscometer; data that are difficult to obtain otherwise. Oils A and B differ in boiling range. In practice, the data were used to determine throughput rates in reactors containing solid catalysts at up to 450°C.

A correlation study of the effects of temperature and pressure on the viscosities of liquids and vapors was made by Smith and Brown<sup>(1)</sup>. Though the correlation is based on low molecular weight hydrocarbons up to hexane, a rough comparison may be made with the present data. The correlation is a plot of  $\eta/\sqrt{M}$  vs. reduced pressure ( $P/P$  critical) with a reduced temperature

( $T/T_{critical}$ ) isotherms. If assumptions are made for a critical pressure of 80 atm, critical temperature of 600°C and an average molecular weight ( $M$ ) of 144, the correlation predicts a viscosity of 0.3 cp at 340°C and 5500 psig for oil B. The measured value for these conditions is 0.2 cp, a fair comparison in view of the extensive extrapolation of the correlation and rough assumptions made for the critical parameters and molecular weight.

The accuracy of density measurements at high temperatures was tested with the pure compound tetralin. The points shown on the graph in Figure 6 were measured experimentally by gamma ray absorption in this densitometer. The curve drawn on the graph was calculated from established equations<sup>(2)</sup> for this particular compound. The agreement is excellent, lending confidence in density measurements on new materials. Densities of various coal oils have been measured from ambient temperature up to 450°C and pressures up to 5500 psig. All show a slow linear decrease of density with temperature of about  $1.25 \times 10^{-3}$  gm/cc per °C in this thermal range.

In conclusion, it has been demonstrated that satisfactory density and viscosity data can be obtained with this gamma ray apparatus, at quite drastic physical conditions.

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Figure 1

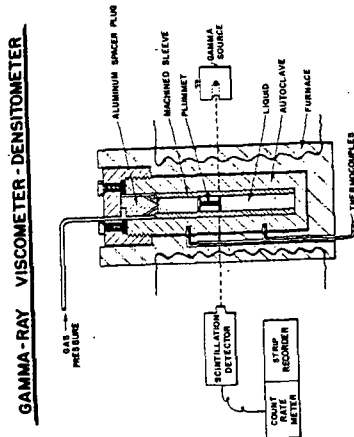


Figure 2

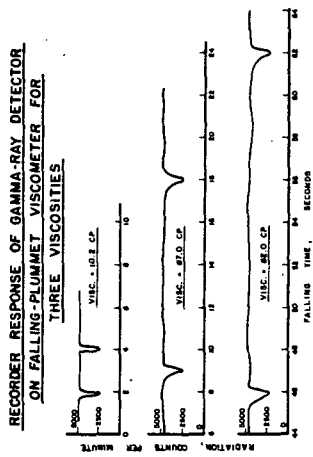


Figure 3

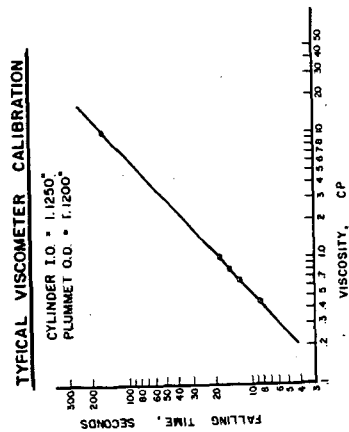


Figure 4

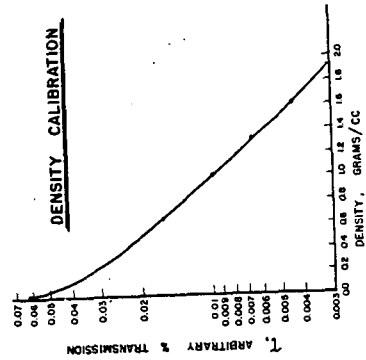


Figure 5

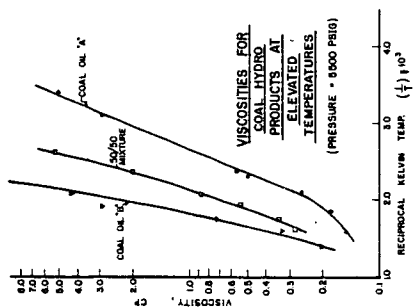
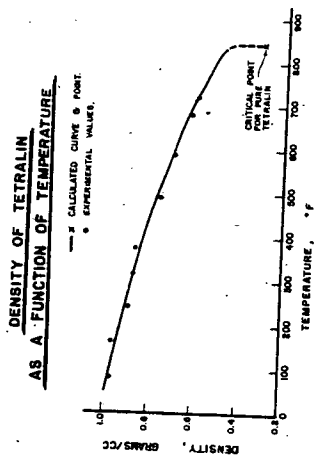


Figure 6



A General Method for the Synthesis of Perdeuterated Hydrocarbons.  
The Syntheses of n-Octane-d<sub>18</sub> and 2,2,4-Trimethylpentane-d<sub>18</sub>.

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### Introduction

As part of a continuing study of the relationship of physical properties to hydrocarbon structure, the changes in the properties when deuterium is substituted for hydrogen in hydrocarbons have been under scrutiny in this laboratory. Earlier, benzene-d<sub>6</sub> and cyclohexane-d<sub>12</sub> were prepared<sup>1</sup> and the properties determined.<sup>2,3,4</sup> The results were sufficiently interesting that the syntheses of a perdeuterated normal paraffin and a perdeuterated branched-chain paraffin hydrocarbon were undertaken.

Although the literature<sup>5,6,7,8</sup> records the preparation of a number of perdeuterated hydrocarbons, none of the procedures appeared to be satisfactory for the synthesis of molar quantities of perdeuterated aliphatic hydrocarbons in the C<sub>6</sub> to C<sub>12</sub> molecular weight range. The reported syntheses may be divided into two broad classes:

- (1) syntheses starting from available chemical intermediates and utilizing classical chemical reactions to construct the desired perdeuterated molecule. An example of this procedure is the synthesis of spiro-pentane-d<sub>8</sub> starting from calcium carbide by House, Lord and Rao.<sup>9</sup>
- (2) syntheses starting from a hydrocarbon possessing the same carbon skeleton as that desired in the final product and involving exchange of the hydrogens of the hydrocarbon with the deuterium atoms in a deuterium-containing molecule, e.g., D<sub>2</sub>O, D<sub>2</sub>SO<sub>4</sub>. The synthesis of benzene-d<sub>6</sub> by Ingold and coworkers<sup>10</sup> is a classical example of this approach.

Group (1) syntheses suffer from the fundamental disadvantage that each hydrocarbon structural-type requires a different synthetic route. Further, as the carbon skeleton of the molecule becomes more complex, the number of synthetic steps frequently increases rapidly. Since group (2) routes do not have these disadvantages, the present effort was confined to developing a procedure of this type but avoiding the problems noted below.

The exchange of deuterium between deuteriosulfuric acid and aromatic hydrocarbons proceeds readily at temperatures where no skeletal changes or other side reactions occur to any significant extent. Unfortunately, with aliphatic hydrocarbons, Setkina and coworkers<sup>11</sup> have found that under mild conditions only the tertiary hydrogens are exchanged. Under forcing conditions the expected carbonium ion rearrangements accompany the exchange.<sup>12</sup> Similarly, Dixon and Schiessler<sup>13</sup>

found that the vapor phase exchange between deuterium oxide and hydrocarbons is attended by significant cracking and/or isomerization.

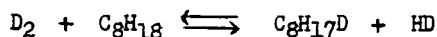
In contrast, Burwell and coworkers<sup>14,15,16,17</sup> in their classical study of the mechanism of hydrogen exchange observed that the exchange of deuterium gas with aliphatic hydrocarbons proceeded rapidly in the vapor phase over metal catalysts and was accompanied by little or no carbon skeletal rearrangements. This procedure suffers only from the disadvantage that for the synthesis of molar quantities of a C<sub>6</sub> to C<sub>12</sub> paraffin hydrocarbon extremely large volumes (of the order of thousands of liters at STP) of deuterium must be used. Since our laboratory, like many others, lacks the facilities for the safe handling and compression of large amounts of hydrogen, a scheme involving the direct deuterium-hydrocarbon exchange but avoiding the handling of large amounts of deuterium was developed.

### The Apparatus

Figure 1 is a flow diagram of the apparatus. A complete description of the apparatus and full experimental details may be found in reference 18.

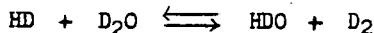
The principal operations occurring in the system are:

- (1) Hydrogen-deuterium gas is continuously circulated through the entire apparatus.
- (2) In the "deuterator" section this gas mixed with hydrocarbon vapor passes over a pelleted nickel on kieselguhr<sup>19</sup> catalyst. A statistical distribution of deuterium and hydrogen atoms between the gas and the hydrocarbon results, e.g.,



The partially deuterated hydrocarbon is then separated by condensation and the hydrogen-deuterium gas passes to the "regenerator" section.

- (3) Here, the hydrogen-deuterium gas mixed with superheated deuterium oxide vapor is passed over the nickel on kieselguhr catalyst. The gas is re-enriched in deuterium from the heavy water



and as the gases leave the "regenerator" the water is separated by condensation while the hydrogen-deuterium gas returns to the "deuterator" section. The hydrogen-water equilibrium constant can be expressed as:<sup>20</sup>

$$\log K = \frac{928}{4.57 T} - 0.1320$$

where

$$K = \frac{[\text{D}_2\text{O}][\text{H}_2]}{[\text{H}_2\text{O}][\text{D}_2]}$$

K is 1.980 at 200° and decreases as the temperature increases. Therefore, the regenerator was maintained at 300° C.

By this technique, the advantages of both the deuterium-hydrocarbon and deuterium oxide-hydrocarbon exchange processes are realized without the disadvantages of either. Although the hydrocarbon was in contact with approximately 1000 liters of deuterium gas during each twenty-four hour period of operation, there were only 12 liters of gas in the apparatus at any given time.

The apparatus was all glass except for the circulation pump which consisted of two counteracting sylvon bellows. Neither the deuterium oxide nor the hydrocarbon came in contact with the pump.

Since the maximum transfer of deuterium from heavy water to hydrocarbon is obtained by passing the hydrocarbon through the deuterator only once per charge of heavy water to the boiler, the following procedure was used. Hydrocarbon was fed slowly from reservoir A, Figure 1, into the incoming deuterium stream. At the entrance to the catalyst chamber the hydrocarbon was vaporized and the mixture of gases passed over the catalyst. On leaving the catalyst the hydrocarbon was separated from the hydrogen by condensation and stored in reservoir C. In contrast, the heavy water was continuously vaporized in the boiler, J, passed over the catalyst in the regenerator, condensed, returned to the boiler, revaporized and so on. When all of the hydrocarbon charge had passed from reservoir A to reservoir C, it was returned to A and a fresh charge of heavy water placed in the boiler, J.

With this procedure the variables which determine the amount of deuterium transferred from the water to the hydrocarbon per charge of heavy water are:

- (1) rate of throughput of the hydrocarbon
- (2) deuterium content of the entering hydrocarbon
- (3) moles of hydrocarbon passed per cycle
- (4) rate of hydrogen-deuterium gas flow
- (5) rate of heavy water flow through the regenerator
- (6) moles of water in the boiler
- (7) deuterium content of the water.

Since the temperature and the rates of throughput of hydrocarbon, hydrogen-deuterium gas and water vapor can be so adjusted that the H-D exchange equilibria are continuously maintained in the deuterator and regenerator catalyst chambers, it is possible to express the rate of decrease of the deuterium concentration of the water with time as a function of the variables listed above.<sup>18</sup> The differential equation was integrated to yield:

$$t = \frac{1}{K} \ln \left( \frac{[\text{HC}] - [\text{D}_2\text{O}_{\text{start}}]}{[\text{HC}] - [\text{D}_2\text{O}_{\text{end}}]} \right)$$

where

t = time for passage of the complete hydrocarbon charge through the deuterator (time of one "cycle")

K = a constant

$[\text{HC}]$  = concentration of deuterium in the hydrocarbon (expressed as the fraction of the H + D atoms that were D) at the beginning of the cycle

$[\text{D}_2\text{O}_{\text{start}}]$  = concentration of deuterium in the water at the start (expressed as the fraction of the H + D atoms that were D)

$[\text{D}_2\text{O}_{\text{end}}]$  = concentration of deuterium atoms in the water at the completion of the cycle (expressed as the fraction of the H + D atoms that were D).

The last quantity is the only unknown and once it is calculated from the equation the number of deuterium atoms transferred from the water to the hydrocarbon can be obtained easily. Thus, the number of equilibrations (or cycles) to obtain any given amount of a hydrocarbon of a given deuterium content may be predicted.

#### n-Octane-d<sub>18</sub>

Using the nickel on kieselguhr catalyst and a deuterator temperature of 115-130°, approximately 100 g. of n-octane-d<sub>18</sub> were synthesized from Phillips Research Grade n-octane. The hydrocarbon was cycled over the catalyst nine times, a fresh charge of heavy water being used for each cycle. The final deuterocarbon was fractionally distilled (14 fractions) and the fractions analyzed by vapor phase chromatography. As shown in Table I, the first fraction contained essentially all the products of cracking and isomerization. This was expected since any product which resulted from cracking or isomerization of n-octane would be lower boiling.

Table I

#### Impurity Concentrations in n-Octane-d<sub>18</sub>

Fraction	Concentration of Impurity in the Fraction (% by weight)	Concentration in the "Crude" Product (% by weight)
1	10	0.2
2	0.2	0.01
3-13	not detectable <0.02	<0.001
Total		~0.2

The isotopic concentrations in fractions 3-13, as obtained by density determination, were 99.1% D, 0.9% H.

#### 2,2,4-Trimethylpentane-d<sub>18</sub>

An attempt was made to synthesize 2,2,4-trimethylpentane-d<sub>18</sub> by the procedure used for the synthesis of n-octane-d<sub>18</sub>. With the same rate of hydrocarbon feed to the catalyst, the product from the first cycle had approximately 30% of the expected deuterium content. Two more cycles through the apparatus did not appreciably increase the deuterium content of the hydrocarbon.

The lack of equilibration was due probably to the phenomenon described by Burwell,<sup>14,15</sup> i.e., that complete equilibration between deuterium and a hydrocarbon molecule on a catalyst surface will not take place past a quaternary carbon atom. The quaternary carbon atom in 2,2,4-trimethylpentane has attached to it a 2-methylpropyl group and three methyl groups. Should the 2-methylpropyl group be chemisorbed on the catalyst surface one-half of the hydrogen atoms in the hydrocarbon molecule will equilibrate with deuterium and the deuterium content will be half that produced by an equivalent chemisorption of n-octane and deuterium. However, chemisorption of the hydrocarbon molecule via a methyl group (the probability of this event is 0.5, on the basis of the hydrogen atoms accessible to the catalyst) will yield a deuterium content one-eighteenth that produced by the equivalent chemisorption of n-octane and deuterium.

An attempt was made to produce equilibration by raising the temperature of the catalyst chamber. Not only would complete equilibration be favored by more frequent adsorption-desorption of the hydrocarbon on the catalyst surface, but the temperature increase would also increase the probability of a methylene type adsorption

suggested by both Burwell<sup>5</sup> and Kemball.<sup>21</sup> Such adsorption would by its nature increase the deuterium content of the molecule.

Equilibrium between deuterium and the hydrocarbon was approached rapidly in the 181-195° range but was accompanied by extensive cracking and isomerization. A temperature of 154-164° was used as a compromise between a rapid reaction with extensive production of impurities and a very slow reaction without.

The apparent "equilibrium constant" of the reaction between deuterium gas and 2,2,4-trimethylpentane in the deuterator at this temperature was 0.3, whereas the equivalent value for n-octane was 2. These values were obtained by analysis of the products from the deuterator and depended, in the case of 2,2,4-trimethylpentane, on the residence time on the catalyst.

Table II

Impurity Concentrations in 2,2,4-Trimethylpentane-d<sub>18</sub>

Fraction	Concentration of Impurity in the Fraction (% by weight)		Concentration in the "Crude" Product (% by weight)
	Cracking	Isomerization	
1	55	< 0.02	1.2
2	10	< 0.02	0.28
3	1.6	< 0.02	0.074
4	0.1	< 0.02	0.0082
5-9	< 0.02	< 0.02	< 0.02
10	< 0.02	0.2	0.017
11	< 0.02	3.2	0.024
residue	< 0.02	5.3	0.11
Total			~1.8

Three isomer impurity peaks were obtained in the vapor phase chromatogram. As the retention times of two of the pairs of octane isomers are almost identical, these three peaks could be due to five isomers. The total concentration of all isomers in the original deuterated product is believed to be less than 0.2% as based on chromatographic results on the fractionated material. The major impurity is probably a deuterated 2,4-dimethylhexane or 2,5-dimethylhexane. Two other isomers, formed in concentrations approximately one-tenth those of the major impurity, were 2,2-dimethylhexane and either 3,3-dimethylhexane and/or 2,2,3-trimethylpentane.

Distillation fractions 5-9 had no isomerization and cracking impurities detectable by vapor phase chromatography and were taken as high-purity deuterated 2,2,4-trimethylpentane. The vapor phase chromatography results indicate that the carbon skeleton of this material is more than 99.9% 2,2,4-trimethylpentane. As determined by density measurements, the isotopic purity of the final product is 97.4% D.

In conclusion, it should be emphasized that the problem of extremely slow equilibration observed with 2,2,4-trimethylpentane is probably confined to molecules possessing quarternary carbon atoms. It is expected that all other types of aliphatic hydrocarbons will behave in a fashion very similar to that of n-octane.

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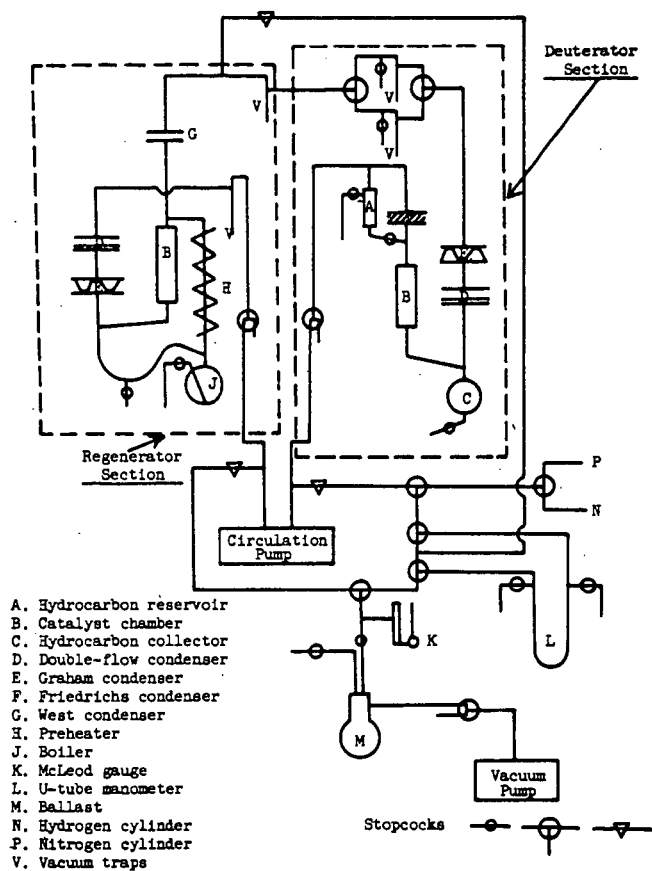


Figure 1. Schematic Diagram of Deuteration Apparatus

EFFECT OF NUCLEAR IRRADIATION  
ON THE ACTIVITY OF  
IRON METHANATION CATALYSTS

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INTRODUCTION

As part of a program to determine the place of nuclear energy and related technology in the utility gas industry, reports were prepared for the Gas Operations Research Committee of the American Gas Association by the Vitro Corporation of America and Arthur D. Little, Inc., on the feasibility of specific nuclear applications.<sup>8</sup> The Little report,<sup>10</sup> "Effects of Radiant Energy on the Synthesis of Gaseous Fuels," suggested three subjects for experimental study: 1) irradiation of catalysts prior to use, with the objective of enhancing their activity for desirable reactions by producing crystal disorders and/or inducing radioactivity, 2) irradiation of catalysts during use to attain objectives similar to 1 above, and to possibly effect beneficial radiochemical reactions, and 3) use of high-frequency discharges or other radiation to produce gas-phase reactions in the absence of catalysts.

A specific study based on the first of these suggestions was initiated at the Institute of Gas Technology in January 1958 to investigate the effects of nuclear irradiation on the activity and selectivity of iron methanation catalysts.

Bombardment of solid materials by nuclear radiation is known to produce a number of physical changes commonly called "defects". A description of the nature of these defects has been given by Dienes,<sup>3</sup> Harwood,<sup>9</sup> and others. Gamma rays, when losing their energy by absorption in a solid, produce primarily three effects: the photoelectric effect, the Compton effect, and positron-electron pair production. In addition, gamma radiation has been observed to produce displaced atoms in solids, but this effect is very small. Heavier particles, such as neutrons, inflict more serious damage to a solid. Neutron bombardment may result in crystal lattice defects, neutron capture, ejection of a charged particle, or nuclear fission. Several types of lattice defects may be produced which include vacancies, interstitial atoms, and impurity atoms. Other effects observed are replacement collisions, thermal spikes, and displacement spikes. Fission of an atomic nucleus or neutron capture, which result from impact with neutrons, produce isotopes or new elements.

All of the radiation effects described are similar in that they affect the electronic configuration in solids. Although much work has been done to relate the electronic structure of solids to their catalytic behavior,<sup>6</sup> most work has been concerned with electronic effects related to factors other than those due to nuclear irradiation. Only a few investigators have studied the effects of nuclear irradiation, primarily X-ray and gamma-ray, on catalyst behavior. Depending on the catalytic system investigated, nuclear irradiation has been observed to result in an increase in activity in some cases, and a decrease in others.

The work of Clarke and Gibson<sup>1</sup> with the Fischer-Tropsch reaction is of special interest in relation to the present methanation study. They observed significant increases in the activity of iron mill scale catalysts which had been treated before reduction with 1 to  $5 \times 10^7$  roentgens of gamma radiation. The increased activity persisted for the durations of their tests, which ranged from 48 to 300 hours. A considerable effect of particle size was established, with increases in activity varying from nil with 400- to 600-micron particles, to 40 to 60 percent with 0.2- to 5-micron particles. These investigators also report that no change in catalyst activity was obtained in a test with a neutron-irradiated catalyst of large particle size (1.2 to 2.4 mm.).

An extensive A.G.A.-sponsored study of the methanation process has been underway at the Institute for some time, in which a highly active Raney nickel catalyst has been brought to advanced stages of development.<sup>4,5</sup> Several types of iron catalysts had been studied earlier, but their use in the development of the methanation process was abandoned, since it was not possible to overcome the tendency of these catalysts to cause high rates of carbon formation at the severe operating conditions favoring methane production.<sup>12</sup> Results similar to those obtained at the Institute with iron methanation catalysts have also been obtained by other investigators, principally the U.S. Bureau of Mines<sup>7</sup> and the British Gas Research Board.<sup>2</sup>

The favorable results obtained by Clarke and Gibson indicated that improvement in iron catalyst properties may be feasible by use of a suitable irradiation procedure. If sufficient activity for methane production in the absence of carbon deposition and higher hydrocarbon formation could be achieved by such treatment, advantage could then be taken of the high sulfur resistance and low cost of iron catalysts. This might make these catalysts attractive alternates to the presently used nickel catalyst. Cobalt catalysts, which have many properties similar to those of iron catalysts, might also benefit from irradiation.

#### EQUIPMENT AND PROCEDURES

Three types of iron catalyst were used in this study. A skeletal iron catalyst was prepared by partial caustic leaching of a crushed, 50% aluminum-50% iron Raney alloy. A catalytically active reduced iron surface was prepared on National Controlled "T" chilled iron shot obtained from the National Metal Abrasives Company. Commercial ammonia synthesis catalyst, sold under the

designation of Aero Catalyst FM-2 by the American Cyanamid Company, was also used.

Gamma irradiation of catalysts was done in the High Level Irradiation Facility of Argonne National Laboratory. Total dosage for each batch was  $10^8$  roentgens at an intensity of approximately  $10^4$  roentgens per minute. Both irradiated and unirradiated Raney iron catalysts were stored at  $0^\circ\text{F}$ . to minimize annealing. Other catalysts were stored at room temperature. The maximum time elapsed between irradiation and use did not exceed one week for the catalysts stored at room temperature, and was less than one month for the refrigerated samples.

The CP-5 Nuclear Reactor at Argonne National Laboratory was utilized for the neutron irradiations. Total dosage for each sample was approximately  $10^{19}$  neutrons per sq. cm. at a neutron flux of about  $2 \times 10^{13}$  neutrons per sq. cm.-sec. Irradiated samples were stored before use at room temperature for approximately one month, to allow the level of induced radioactivity to decay to a safe value.

### Catalyst Testing Apparatus

Both fluid- and fixed-bed reactors were used. Initial tests were made with fluid-bed units, but the reproducibility obtained with this equipment was not sufficient to permit accurate measurement of changes in catalyst activity caused by gamma irradiation. A fixed-bed reactor was therefore constructed and used for all subsequent tests. Flow diagrams of both types of reactors are shown in Figure 1.

Fluid-Bed Unit. The fluid-bed unit, as shown on the left in Figure 1, was constructed in duplicate, except for the purification section, to permit simultaneous testing of unirradiated and irradiated catalysts. Each reactor consisted of an 18-in. high pyrex catalyst section, 30 mm. O.D. by 26.4 mm. I.D., surmounted by a 103-mm. O.D. by 15-in. high catalyst separation zone. A 6-in. long by 25-mm. O.D. section below the catalyst section, packed with 3-mm. O.D. pyrex tubing, served as an inlet gas preheater. A porous glass disk separated the preheat and catalyst sections, and acted as a catalyst bed support and a feed gas distributor. Product gas was withdrawn through an 8-in. long, tubular, porous glass filter which retained the catalyst fines. The reactor and preheat section were completely enclosed in a single Hevi Duty electric furnace. Temperatures were measured with five 20-ga. chromel-alumel thermocouples inserted in a 10-mm. O.D. thermowell axially located in the reactor. Power to the electric furnace was controlled manually.

Synthesis gas and purge nitrogen were fed from high-pressure cylinders through activated carbon to remove sulfur compounds. Dry test meters were used for metering of feed gases, and wet test meters for the product gases.

Fixed-Bed Unit. The fixed-bed unit was essentially the same as the fluid-bed, except for the reactor itself, shown at the right in Figure 1. The reactor consisted of a 16-3/4 in. long, 1-1/2 in. IPS, Schedule 80, stainless steel pipe press-fitted into a 12-in. long by 5-in. O.D. aluminum bronze block.

The block was spirally wrapped with resistance heating wires. A 3/8-in. O.D., 20-ga. stainless steel thermowell was mounted axially in the reactor and extended its full length. Feed gases entered at the top of the reactor and flowed downward through the catalyst bed. The bed was confined between two 24-mesh type 304 stainless steel screens. The space above the catalyst bed was packed with reagent grade copper shot to facilitate inlet gas preheating. The lower part of the reactor was packed with -18, + 20 mesh size, refined glass beads instead of copper shot to minimize heat losses. The bottom of the reactor was flanged to facilitate catalyst charging.

When radioactive catalysts were tested, a thin stainless steel liner was used to prevent reactor contamination. The liner, which was 16 in. long, 1.375 in. O.D. and 1.278 in. I.D., was closed at the bottom by a perforated stainless steel plate, and was held in the reactor by means of a 1-in. long threaded section at its top.

Test Procedures. Synthesis gas consisting of hydrogen and carbon monoxide in a 3:1 mole ratio was purchased in high-pressure cylinders. Electrolytic grade hydrogen was blended with this mixture for tests in which higher  $H_2/CO$  ratios were used for the feed. Feed and product gas compositions were determined by mass spectrometer.

With all of the catalysts studied, some preliminary treatment was required after the catalyst sample was placed in the reactor and before the methanation test was started. The Raney catalysts were reduced in the catalyst-preparation procedure and transferred to the reactor under methanol. The bed was then heated and a stream of nitrogen was passed through it, to thoroughly dry the catalyst prior to the methanation test. Iron shot and ammonia synthesis catalysts were charged to the reactor in the oxidized state and were reduced with hydrogen prior to the methanation tests.

There was little difference in test procedure between the fluid- and fixed-bed units except for the size of catalyst samples, and gas flow rates. In the fluid-bed reactor, the catalyst charge was approximately 100 c.c., occupying about 11 in. of the reactor height when fluidized. A 1-1/8-in. deep bed, with a volume of 30 c.c., was used in the fixed-bed reactor tests on gamma-irradiated Raney and ammonia synthesis catalysts. In tests of neutron-irradiated ammonia synthesis catalyst, where the reactor liner was used, the depth of the 30 c.c. sample was 1-9/16 in. A 100 c.c., 3-3/4 in. deep, bed was required for the tests with iron shot because of its low activity.

## DISCUSSION

Operating conditions for evaluation of the relative methanation activity of irradiated and unirradiated iron catalyst samples were limited to a narrow range because 1) iron catalysts have a lower activity for the methanation reaction than nickel catalysts, 2) methane formation is greatly exceeded by higher hydrocarbon formation at the lower temperatures, and 3) methane formation is accompanied by considerable carbon formation at the higher

temperatures. Carbon deposition was most detrimental in these tests, since rapid buildup of carbon on the catalyst surface made detection of changes in catalyst performance resulting from other causes, such as irradiation, exceedingly difficult. Under some conditions, carbon deposition was so severe that the catalyst bed was almost completely blocked to gas flow. It was determined experimentally to be impractical, for this reason, to feed synthesis gas having a hydrogen to carbon monoxide ratio of less than 6:1 to the fixed-bed reactor, or less than 9:1 to the fluid-bed reactor. The resulting product gases consequently contained large concentrations of excess hydrogen, which is undesirable in the methanation process, but should not affect the validity of the activity tests. Although other investigators have shown that steam dilution can be used effectively to control carbon deposition, steam feed was not practical in these tests because of possible reduction of the already low carbon monoxide content by the water-gas shift reaction.

Since increases in catalyst temperature will 1) increase carbon deposition, 2) increase the rate of methane formation, and 3) decrease the equilibrium methane concentration in the product gas, the selection of a suitable temperature level was of major importance. Reactor temperatures (and thus catalyst activities) were kept as low as possible within the limits of accurate gas flow and gas composition measurements. The fluid-bed reactor was particularly inflexible in this respect, since gas velocity had to be maintained within narrow limits to keep the catalyst fluidized. Therefore, low catalyst activity could not be independently compensated by a low synthesis gas space velocity to obtain a specific degree of carbon monoxide conversion.

#### Effects of Gamma Irradiation

To determine the effect of prior gamma irradiation of the catalyst on the conversion of carbon monoxide to methane, conditions of synthesis gas space velocity and catalyst bed temperature were selected for each type of catalyst tested so that the resulting product gas composition was considerably removed from the equilibrium value. Sets of comparison tests were made with irradiated and control samples from the same catalyst batch at equal operating conditions. Differences in catalyst activity were noted by comparison of the methane-equivalent space-time yields (the rate of production per unit volume of catalyst of the total gaseous hydrocarbons times their average carbon number) from each set of tests.

Results of three runs made with Raney iron catalyst in the fluid-bed methanation unit are given in Table 1. In these tests a space velocity of approximately 1000 SCF (standard cubic foot of gas at 60°F., 30 in. Hg, saturated with water vapor) per cubic foot of catalyst per hour was employed, with a 9.5-9.7:1.0 H<sub>2</sub>/CO ratio synthesis gas. The reactor temperature was maintained at 500°F. Under these conditions, carbon recovery as gaseous products varied between 72 and 93 wt. %, corresponding to carbon deposition on the catalyst between 7 and 17 wt. % of the carbon fed.

Table 1.-FLUID-BED REACTOR TESTS  
WITH RANEY IRON CATALYST (75% ALUMINUM CONVERSION)

Run No.	12A	13	12B
Reactor No.	1	2	2
Catalyst No.	6A	6A	6B
Catalyst Treatment	Control	Control	Irradiated
Carbon Recovery, wt. %	83	85	93
Methane/Higher			
Hydrocarbon Mole Ratio	2.0	2.1	2.2
Methane Equivalent Space-Time			
Yield, SCF/cu. ft. cat.-hr.	32	19	64

The results of these tests, which were made with samples from the same catalyst batch, indicate that the gamma-irradiated catalyst produced more than twice as much methane equivalent per unit of catalyst and time as the unirradiated catalyst. However, no firm conclusions could be justified regarding the actual degree of catalyst improvement, because of the limited reproducibility of results from the fluid-bed reactor. The poor reproducibility was attributed to the large number of operating variables (not necessarily related to intrinsic catalyst activity) which could not be controlled within sufficiently narrow limits. Control of temperature gradients in the bed was especially difficult.

To minimize the effect of extraneous variables in the methanation test procedure, further comparisons between irradiated and unirradiated catalyst were made in the fixed-bed reactor. In addition to better control of process variables with the fixed-bed unit, the elimination of fluidization requirements made possible the selection of catalyst particle size, sample size, bed temperature, and space velocity to give the desired degree of conversion with catalysts having widely different activities, without alteration of the reactor or feed and product gas trains.

The results of three runs made with Raney iron catalyst in the fixed-bed reactor are given in Table 2. This catalyst differed from that used in the fluid-bed tests in particle size range, and in that only 30% of the aluminum was reacted during catalyst activation, as compared with 75% with the fluid-bed catalysts.

Table 2.-FIXED-BED REACTOR TESTS  
WITH RANEY IRON CATALYST (30% ALUMINUM CONVERSION)

Run No.	19	16	24
Catalyst No.	13A	13B	15
Catalyst Treatment	Control	Irradiated	Alloy Irradiated
Carbon Recovery, wt. %	86	88	88
Methane/Higher			
Hydrocarbon Mole Ratio	5.2	4.6	3.2
Methane Equivalent Space-Time			
Yield, SCF/cu. ft. cat.-hr.	41	46	39

Runs 16 and 19 were made with irradiated and unirradiated samples, respectively. Run 24 was made with a catalyst prepared from Raney alloy which had been irradiated prior to catalyst activation, in contrast to irradiation of the activated catalyst in each of the other Raney catalyst tests. A feed gas space velocity of approximately 2000 SCF/cu. ft. catalyst-hr of 6.4-6.9:1.0  $H_2/CO$  synthesis gas was employed, with a catalyst bed temperature of 700°F. Carbon recovery as gaseous products ranged between 86 and 88 wt. % at these conditions. Comparing the results from Runs 16 and 24 with those from Run 19, it can be seen that the methane-equivalent space-time yield was about 12% higher with the irradiated catalyst, whereas it was about 5% lower when the Raney alloy was irradiated prior to catalyst activation. These variations in catalyst activity are relatively small, and approach in magnitude the reproducibility of the test. However, the increase in the activity of the irradiated Raney iron catalyst was consistent with the results obtained earlier in fluid-bed operation.

Two runs were made with iron shot catalyst. However, the level of activity of this catalyst was so low, and concentrations of hydrocarbons in the product gas were so small, that no significance could be placed on the comparative data from these runs.

The only commercial catalyst employed in this study was the ammonia synthesis catalyst, which had a level of activity comparable with that of Raney iron. Test conditions were the same as those for the fixed-bed tests with Raney iron, except that the catalyst bed temperature was maintained at 500°F. As shown in Table 3, an increase of approximately 10% in methane-equivalent space-time yield was observed with the gamma-irradiated sample; this is similar to the increase found with Raney iron.

No evidence was found to indicate that the synthesis reaction mechanism was significantly affected by prior gamma irradiation of the catalyst. Carbon deposition and distribution of products between methane and higher molecular weight hydrocarbons did not vary in any systematic manner which could be attributed to catalyst irradiation. All of the tests were of short duration, so it could not be determined whether the initial effects observed would persist with longer use of the catalyst.

Since the results were obtained with catalysts which had been irradiated at least one day prior to test, they are not indicative of the possible effect of irradiation immediately prior to or

Table 3.-FIXED-BED REACTOR TESTS  
WITH AMMONIA SYNTHESIS CATALYST

Run No.	25	26
Catalyst No.	22	23
Catalyst Treatment	Control	Irradiated
Carbon Recovery, wt. %	86	87
Methane/Higher		
Hydrocarbon Mole Ratio	0.5	0.4
Methane Equivalent Space-Time		
Yield, SCF/cu. ft. cat.-hr.	39	43



during the methanation reaction, where short-lived effects might be significant.

The residual effects of high-intensity gamma radiation on solids are limited to ionization and possibly slight crystal lattice defect production. X-ray diffraction examination of an irradiated sample of Raney iron catalyst failed to disclose any evidence of crystal lattice deformation by the radiation dosage of  $10^8$  roentgens employed in this study. This does not mean that defects were not produced during the gamma treatment, but that any physical effects on the crystal were too small or too short-lived to be detected by subsequent X-ray diffraction analysis.

#### Effects of Neutron Irradiation

Four comparative tests with samples of ammonia synthesis catalyst were made to determine the effect of thermal neutron irradiation on catalyst activity. A summary of the results of these tests is given in Table 4.

Runs 27 and 30 were made with samples of untreated ammonia synthesis catalyst; Runs 28 and 29, with irradiated samples. The run conditions employed were the same as those used in comparative tests of gamma-irradiated ammonia synthesis catalysts: 2000 SCF/cu. ft. catalyst-hr feed gas space velocity, 6:1 hydrogen/carbon monoxide feed gas ratio, and 500°F. catalyst bed temperature.

One sample of irradiated catalyst (No. 25, Run 28) showed an activity that was about 30% higher than the average of the activities of the two untreated samples. A second sample of neutron-irradiated catalyst (No. 26, Run 29) showed an activity substantially the same as that of the unirradiated samples. This difference in activity between the two samples of irradiated catalyst cannot be attributed to any apparent differences in test conditions or method of catalyst reduction. However, in spite of the close control of experimental procedures, the neutron-irradiated sample showing the high catalytic activity (No. 25) appeared to undergo a greater degree of reduction during activation; from the three samples showing similar activity (Nos. 24, 26 and 27), 49.0 to 51.4% of the oxygen content of the iron oxides was removed, whereas with Sample 25 oxygen removal was 71.0%. Work reported by Simnad<sup>11</sup> showed that the rate of reduction of nickel oxide by hydrogen at 250°-350°C is increased by a factor of three when the oxide has been irradiated with high-energy protons.

Table 4.-FIXED-BED REACTOR TESTS OF THERMAL  
NEUTRON-IRRADIATED AMMONIA SYNTHESIS CATALYST

Run No.	27	28	29	30
Catalyst No.	24	25	26	27
Catalyst Treatment	Control	Irradiated		Control
Carbon Recovery, wt. %	87	79	79	80
Methane/Higher Hydrocarbon Mole Ratio	0.34	0.44	0.44	0.42
Methane Equivalent Space-Time Yield, SCF/cu. ft. cat.-hr.	29	36	26	27

Catalysts 25 and 26 were irradiated simultaneously; however, No. 25 was exposed to a neutron flux of  $2.6 \times 10^{13}$  neutrons/sq.-cm.-sec., whereas No. 26 was exposed to a flux of  $2.0 \times 10^{13}$  neutrons/sq.-cm.-sec. The total dosage for Catalyst 25 was therefore 30% greater. The half-lives of the radioactive isotopes of iron present ( $\text{Fe}^{55}$  and  $\text{Fe}^{59}$ ) are 2.94 years and 45.1 days, respectively, with  $\text{Fe}^{55}$  comprising approximately 70% of the total radioactive isotopes present. Since only three days elapsed between the tests with the treated samples, the differences in their catalytic activity should not be due simply to a decrease in radioactivity or to annealing of defects in this period.

The results of these tests indicate that thermal neutron irradiation of ammonia synthesis catalyst prior to use may have an effect on its activity. There was no measurable change, however, in carbon deposition and distribution of products between methane and higher molecular weight hydrocarbons.

Since an increase in catalytic activity was observed with the irradiated sample which had received the higher neutron dosage, it is possible that higher dosage levels than employed in these tests might result in substantially increased catalytic activity. Irradiation by fast neutrons might also increase activity, since a higher ratio of crystal lattice defects to induced radioactivity would be produced.

#### CONCLUSIONS

It can be concluded from the experimental results that gamma irradiation or thermal neutron irradiation prior to use may have a beneficial effect on the activity of iron methanation catalysts. The scope of this program was not sufficient, however, to define the radiation requirements to obtain optimum beneficial effects. The observed degrees of catalyst improvement resulting from irradiation can be considered small from a practical standpoint, in view of the generally low activity and poor product distributions obtained with the iron methanation catalysts studied.

The nature of the improvement due to irradiation seemed to be limited to increased activity with no apparent change in the product selectivity (methane/higher hydrocarbon ratio). No significant decreases in carbon deposition were obtained. Although direct analogy cannot be drawn, the observed results with gamma-irradiated catalysts do not appear to differ greatly from the findings of Clarke and Gibson with iron mill scale catalyst.<sup>1</sup>

Although this study was limited to tests of short duration, and to limited ranges of radiation intensity and dosage levels, the results show that a more detailed fundamental investigation in this area would be warranted. Further study should include the testing of other types of methanation catalysts, other catalyst particle sizes, other forms of nuclear radiation, and other radiation dosage and intensity levels.

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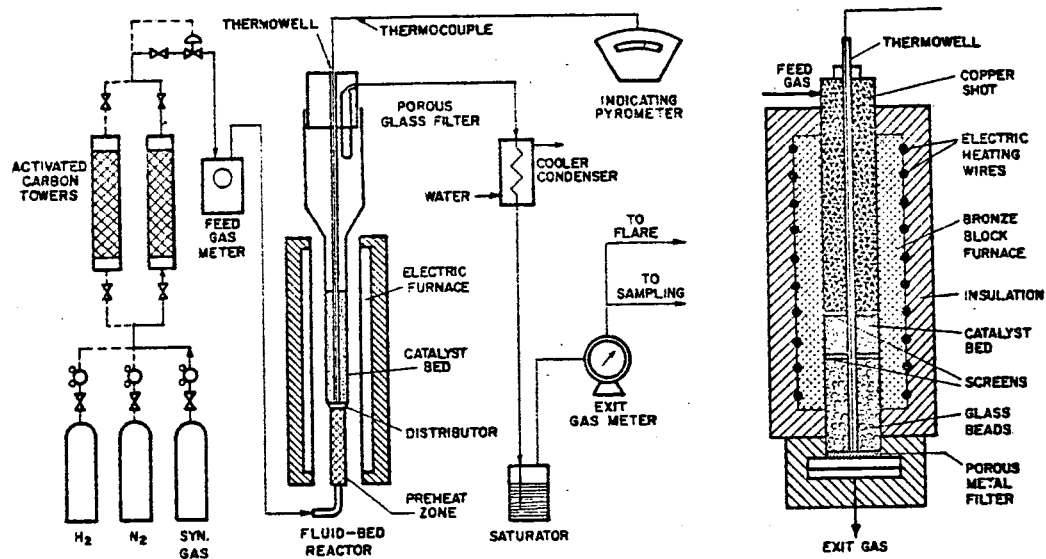
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Fluid-bed Reactor Unit

Fixed-bed Reactor

Figure 1. Methanation Catalyst Testing Equipment

# The Use of Radioactive Tracers in Studying Functional Groups in Coals

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In the classical organic chemical method of elucidating the structure of an unknown substance reactions are carried out with reagents that would be expected to react only with one kind of functional group or in some other specified way. The product is purified from excess reagent and by-products, for example by crystallization to constant melting point; it is then analysed and characterized by further specific reactions. Thus if the original substance were a secondary alcohol, it might be oxidized selectively to a ketone, and the character of this established, after purification, by conversion to a phenylhydrazone.

In the chemical study of coal it is not easy to find selective reagents. Different functional groupings in coal often have similar reactivities. Moreover, a single type of group may exhibit a spread of reactivity owing to its occurrence in the coal in a variety of environments; consequently attempts to achieve completeness of reaction usually incur a loss of selectivity. The only purification of reaction products possible, since coal is an involatile solid and only partly soluble, is washing with some suitable liquid to remove excess reagent. Inadequate purification often causes serious difficulties, since in many reactions it has proved impossible to remove adsorbed or otherwise strongly held reagent (for example, chloromethylation catalysed by stannic chloride<sup>1</sup>, dehydrogenation with benzoquinone<sup>2</sup> and triphenylmethyl perchlorate<sup>3</sup>, reduction with lithium and aliphatic amines<sup>4</sup>). Consequently characterization of the product by elementary analysis is made difficult or impossible; other properties, such as the infra-red spectrum may also be affected.

It is the purpose of this paper to develop and illustrate the thesis that some at least of the difficulties outlined above can be obviated by the judicious use of reagents labelled with radioactive atoms. Neutron activation analysis, in which tracer atoms are generated *in situ* by suitable irradiation, might be useful in coal research, for example in determining the silicon content of trimethylsilyl ethers<sup>5</sup>; however this type of analysis is a special case and will not be discussed further (in any case it has not yet been applied to coal so far as the author is aware).

It is difficult to classify in any rational manner possible applications of tracer techniques to organic chemical studies of coal. Therefore three researches in which tracers were used will first be described briefly and the advantages of the technique in these cases will be analysed. Subsequently attention will be drawn to a number of other reactions where the technique would be valuable. It is hoped thus to show inductively the range of application.

## 1. Carbonyl and Hydroxyl Groups

The interpretation of the band at  $1600\text{ cm}^{-1}$  in the infra-red spectra of coals as due in part to the presence of carbonyl groups<sup>5</sup> has been sharply contested<sup>6</sup>. But if it can be shown on other evidence that these groups are present, then the spectra indicate that they must be strongly conjugated and probably chelated to hydroxyl. Carbonyl groups of this type either do not react or react abnormally with the usual reagents<sup>7</sup>; attempts to determine carbonyl in coal with hydroxylamine<sup>8</sup> and

\*The author is indebted to Dr. P. S. Skell for this suggestion.

phenylhydrazine<sup>9</sup> proved unsatisfactory. Treatment with lithium aluminum hydride produced no detectable change, probably because the hydroxy groups formed were re-oxidized very readily during working up of the product.

Given and Peover<sup>10</sup> therefore used radioactive tracer technique with coal extracts in what was essentially a reductive acetylation reaction, the reduction being carried out by electrolysis in dimethylformamide solution. Quinones reduced in this way yield the dianions of the hydroquinones, which react rapidly at room temperature with acetic anhydride to give the hydroquinone diacetates and acetate ions. An extract acetylated with unlabelled reagent was reduced at a stirred mercury cathode controlled at a series of standard potentials against a reference electrode; in this way the reducing power of the system could be varied at will. The quantity of electricity passed was measured with a coulometer. When the current had fallen nearly to zero <sup>14</sup>C-labelled acetic anhydride was added. The product was isolated, washed with unlabelled acetic acid and water to remove adsorbed radioactive acid, and the disintegration rate counted. Counting was continued until about 10,000 had been recorded. The count rate was 2000-8000 min.<sup>-1</sup>.

When acetylated but unreduced materials were treated in DMF with labelled anhydride the count rate of the product was about 90 min.<sup>-1</sup>. Hence neither adsorption of <sup>14</sup>C-acetic acid nor ester exchange with <sup>12</sup>C-acetyl was significant. A further confirmation of this was obtained by determining first the hydroxyl content radiochemically, with the result: O as OH = 4.9%. The radioactive product was then reductively acetylated, again with labelled anhydride. The final count rate gave: total O as OH + CO = 9.3%; hence, by difference, O as CO = 4.4%. The latter value is to be compared with the value 4.0% obtained by direct radiochemical determination as described above on a separate sample of the same extract. Over 90-95% of the radioactivity of the various products was removed by hydrolysis with sulfuric acid, showing that no significant C-acetylation occurred.

Thus the use of tracer technique provided:

1. unequivocal proof that fresh hydroxyl groups are produced by reduction, that is, that carbonyl groups are present
2. an easy means of checking the absence of a possible side-reaction
3. a simple routine method of studying the variation of carbonyl content with fraction of coal extracted and rank of coal
4. simple means of following the distribution of carbonyl groups as a function of their reduction potentials
5. a check on the selectivity of the reduction.

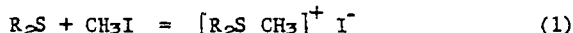
Points 4 and 5 merit some further comment. A "carbonyl content" could be calculated not only from the <sup>14</sup>C-acetyl content but also from the number of coulombs consumed; both were plotted against the controlled potential (see example in Fig. 1). The coulometric figure was somewhat higher than the radiochemical at potentials up to about -1 volt (measured against mercury pool in 0.1N tetraethylammonium iodide as reference electrode). Moreover whereas the radiochemical figure levelled off to an approximately constant value at potentials in the range -1 to -1.4 volt (varying with the coal), the coulometric increased without limit. Hence other groups than carbonyl were reduced, particularly at higher potentials; these were presumably aromatic nuclei. Also shown in Fig. 1 is an approximate distribution curve for radiochemical carbonyl content as a function of reduction potential, from which some deductions about the nature of the carbonyl groups can be made (see ref. 10 for details). In conclusion, it must be admitted that comparison of the infra-red spectra of the coal extracts and their acetylated and reductively acetylated products introduced some uncertainty in the interpretation of the data for carbonyl contents. Depending on the view one takes of the significance of the spectra, the carbonyl contents of extracts of bituminous vitrains of carbon content 78-89% are either in the range 2.2-0.9 or 4.4-1.8% O as CO (decreasing with increasing rank). In either case 65-90% of the oxygen was accounted for as OH + CO.



Since this work was done, it has been shown<sup>11</sup> that finely ground whole coals can be reduced in suspension in DMF. It would therefore be worth applying the radiochemical technique for carbonyl determination to coals; this has not yet been tried. If the conventional reductive acetylation technique (refluxing with zinc, acetic acid, etc.) were applied to acetylated coal using labelled reagents, ester exchange would certainly occur and invalidate the results; however it would be possible to use labelled reagents for both steps, and determine carbonyl by difference. 57.

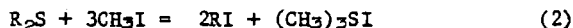
## 2. Sulfur in Coals

It is commonly supposed that the organic sulfur in coals is present in any or all of the forms, mercaptan, disulfide, sulfide, thiophene ring system; the last two, on grounds of superior stability, are the most probable<sup>12</sup>. Of these four forms the first three react (at varying rates) with methyl iodide to form tertiary sulfonium iodides<sup>12</sup>. The primary reaction with a sulfide is:



With mercaptans and disulfides hydrogen iodide and possibly other by-products are also formed.

Selker<sup>13</sup>, in a study of sulfur in vulcanized rubber, showed that further reaction can occur, involving a metathesis of the radicals attached to sulfur, by dissociation and re-methylation; the rate of reaction varied widely with the nature of R. The overall result is:



Thus, when applied to coal, by reaction (1) one methyl group and one iodide ion are introduced for each sulfur atom present as sulfide, whereas by reaction (2) two covalently bound iodine atoms are added to the coal and one molecule of trimethylsulfonium iodide released into solution for each sulfur atom present; in the latter case the sulfur is removed from the coal.

Reaction with methyl iodide has been used by various authors<sup>14-16</sup> to obtain a distribution between the reactive and unreactive forms of sulfur. Kavcic<sup>14</sup> and Angelova<sup>15</sup> assumed that only reaction (2) took place, and measured the decrease in sulfur content. Postovskii and Harlampovitch<sup>16</sup> assumed only reaction (1) and measured the iodine content of the treated coal.

Experiments have been started<sup>17</sup> with the object of finding out which reaction is in fact followed, using <sup>14</sup>C-labelled methyl iodide. The coal is heated at 125° with the iodide in acetone. The product after washing with acetone is analysed for <sup>14</sup>C, and for total S and I by chemical analysis; a sample is washed with sodium nitrate solution and the iodide ion released by exchange is determined by titration. The results still require some clarification, but it is already evident that both reactions (1) and (2) occur, since some sulfur is removed, and both covalent iodine and <sup>14</sup>C-methyl groups are added; there is some exchangeable iodide ion in the products.

A complex reaction like this can obviously only be elucidated by setting up a complete weight balance for methyl, bound and ionized iodine, and sulfur. Radiochemical methods cannot be used for the sulfur, and are hardly necessary for the iodine, since its atomic weight is high and chemical analysis is reasonably accurate (though perhaps slower than radiochemical). However the carbon and hydrogen added as methyl could not feasibly be determined in any other way than by means of tagged atoms.

Perhaps it is worth mentioning for completeness that Ceric has carbonized a series of coals in the presence of added <sup>35</sup>S-enriched pyrite<sup>18</sup>; she found that some of the sulfur released by the pyrite becomes fixed in the organic part of the char. She also used the same tracers in studying the effect of carbonizing in a stream of

hydrogen, steam and ammonia.

### 3. Depolymerization of Coal

The depolymerization of coal with the phenol/boron trifluoride complex studied by Hередy and Newworth<sup>19</sup>, illustrates another use of tracers. In this reaction, the Lewis acid brings about the splitting of linkages of the diarylmethane type, and one molecule of phenol adds across each broken bond. The coal is broken down into products of relatively low molecular weight, a large fraction being soluble in organic solvents. The use of  $^{14}\text{C}$ -labelled phenol permits the amount added to the fragments to be easily determined. The results, in conjunction with the molecular weights of fractions and other data, suggest interesting conclusions about coal structure and in particular the way in which aromatic nuclei are linked together.

### 4. Suggested further Applications

(a) Performic acid oxidation. Early experiments<sup>1</sup> showed that the extent of oxidation of a coal, measured by elementary analysis and by the solubility of the product in caustic soda, was much reduced if the coal was first acetylated. This result, if correct, is important, because it implies that the initial attack of the reagent is on the aromatic nuclei, rather than aliphatic groupings, as might have been expected. However later experiments<sup>20,21</sup> did not confirm the result, and it was suspected that since they were on a larger scale and a higher temperature was reached owing to the strongly exothermic nature of the reaction, the acetyl groups were removed by hydrolysis in the strongly acid reagent. The use of  $^{14}\text{C}$ -acetylated coal would provide the easiest means of testing this hypothesis.

(b) Dehydrogenation of Coals. Peover<sup>2</sup> found that the main reaction between coal macerals and benzoquinone was hydrogen abstraction from hydroaromatic rings and reduction of the quinone to hydroquinone. However, some Diels-Alder addition of quinone to the coal occurred, and consequently the analytical data were difficult to interpret. Interpretation would be easier if the quinone were labelled with  $^{14}\text{C}$ , or perhaps tritium.

(c) Other reactions. There are many other reactions where tracer techniques would greatly assist interpretation of the results, such as oxidation with perbenzoic anhydride<sup>1</sup>, reduction with lithium in ethylene diamine<sup>4</sup>, and bromination with N.bromosuccinimide.

### Conclusions

It is evident from the foregoing that tracer techniques are extremely useful in elucidating the reactions of coal, which are often complex. In particular the techniques offer the best and sometimes the only practicable means of finding out whether a reagent has added to the coal; this addition may be desired or undesired. In any event quantitative data are readily obtainable.

Where the facilities of a radiochemical laboratory are already available, the technique should clearly be used extensively. Provided a counting chamber of the hemispherical or cylindrical types is available, the radioactive reagent can be very heavily diluted with inactive material while still retaining an adequate count rate in the reaction product. Given and Peover in their reductive acetylation experiments<sup>10</sup> only had available an end-window type of counter, so that 1 mc. of  $^{14}\text{C}$ -acetic anhydride could be diluted only to about 20 ml. Where one of the high-efficiency counting chambers is available, 1 mc. could be diluted to many litres; at this dilution 20 ml. reagent used in an acetylation would cost considerably less than a chemical acetyl determination carried out by a commercial microanalytical laboratory. Radiochemical methods therefore may prove not only convenient and useful, but perfectly practicable for extensive use.

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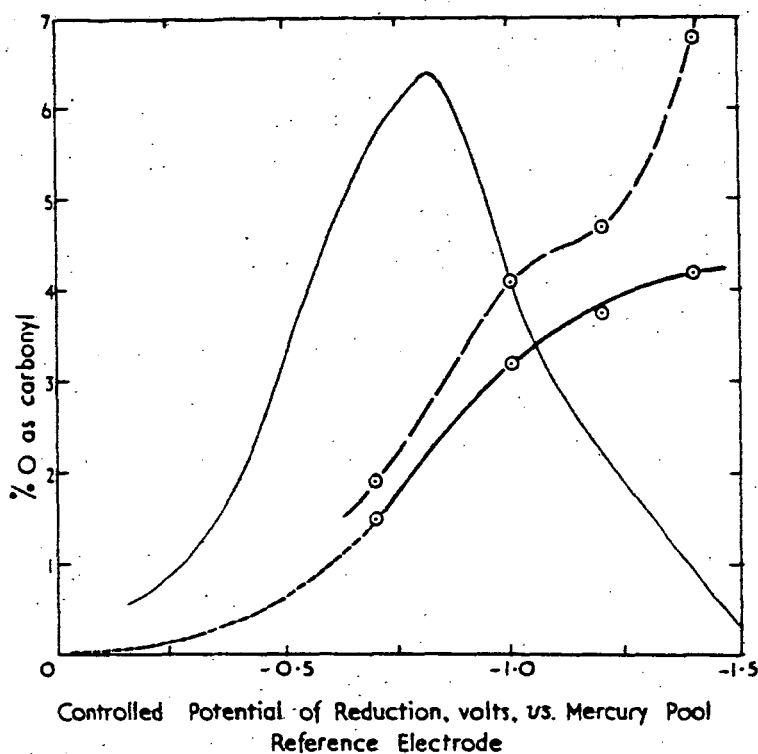


FIG. 2 Variation of apparent carbonyl contents of pyridine extract of coal DIII with potential.

- Radiochemical figures.
- - - Coulometric data, assuming all carbonyl quinonoid.
- Approximate distribution curve of carbonyl content with potential.

# THE STUDY OF CARBON-OXYGEN SURFACE COMPLEXES USING $O^{18}$ AS A TRACER\*

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When  $O_2$  reacts with carbon, CO and  $CO_2$  are the gaseous reaction products. However, not all of the  $O_2$  consumed appears in the form of these products. Some of the oxygen remains chemically bound to the carbon surface in the form of an oxygen surface-complex. To define the mechanism of the carbon-oxygen reaction, the nature of this complex must be more fully understood. For the investigation of the role of these complexes, techniques have been developed whereby the reaction can be studied using low  $O_2$  gas pressures in conjunction with relatively high carbon surface areas<sup>1,2</sup>. Under these conditions, the effect of the formation of a given amount of surface complex is greatly magnified.

In studying the reaction between Graphon and  $O_2$  in the pressure region below 0.1 Torr,\* it has been found that only a small fraction of the total BET surface area of the Graphon is capable of chemisorbing oxygen (less than 2%)<sup>2</sup>. The extent of this chemisorbing area is dependent upon the pretreatment of the Graphon sample and reaction temperature. A fraction of the  $O_2$  consumed continuously goes into this chemisorbed surface complex until the complex coverage reaches a "saturation" value. After saturation is reached, most of the reacting  $O_2$  appears in the form of gaseous reaction products. The complex thus formed is stable in that it will remain on the carbon surface, at reaction temperature, in vacuo (ca.  $10^{-5}$  Torr). To remove this surface complex, it is necessary to heat the carbon to temperatures greater than the reaction temperature. Upon heating of the carbon to a selected higher temperature, the complex decomposes into CO and  $CO_2$ ; the rate of this decomposition decaying from an initially large value to an immeasurably low value.

Among the points in question concerning the behavior of the surface complex, some can be answered by the use of isotopic tracer techniques. In particular, this investigation was undertaken to clarify two main points - (1) the importance of the oxygen surface complex as an intermediate in the conversion of  $O_2$  to CO and (2) the possible relation between the time of formation of the complex and its ease of removal upon outgassing at higher temperatures following reaction.

## EXPERIMENTAL

**Materials Used** - The carbon used in this investigation was Graphon, which was produced by the heat treatment of the channel black, Spheron 6<sup>3</sup>, to 2800°C. Since the surface capable of chemisorbing oxygen increases rapidly with small amounts of oxidation in the low burn-off region, the samples were preoxidized at 650°C. at an  $O_2$  pressure of 0.5 Torr to 14.4% burn-off. Oxidation of the original Graphon to this burn-off increased the BET surface area from 76 to 98 m.<sup>2</sup>/g. Following this substantial amount of burn-off, there was a negligible change in active surface area

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\*\* 1 Torr = 1 mm of mercury.

with the small, additional amounts of oxidation resulting from the present study. The preoxidized Graphon samples were outgassed at 950°C. in vacuo (ca.  $10^{-5}$  Torr) for 3 hrs. prior to each run.

The  $O_2$  enriched in  $O^{18}$  was obtained from the Weizman Institute of Science, Rehovoth, Israel. This oxygen contained 98.4 atomic %  $O^{18}$  (96.8 mole %  $O_2^{18-18}$ ), 0.6 atomic %  $O^{17}$ , and 1.0 atomic %  $O^{16}$ .

**Apparatus** - Figure 1 shows the apparatus used in this investigation. The Graphon sample is placed in a 10 by 60 mm. Vycor test tube which rests in the bottom of a 2 by 35 cm. Vycor reactor. The volume of the reactor system is 0.79 l.; the reservoir has a volume of 4.9 l. The reactor is evacuated by a diffusion pump. McLeod and thermocouple gages are used for pressure measurements. The reactor is heated by a resistance furnace, with furnace temperature regulated by an automatic temperature recorder-controller. The entire apparatus is directly connected through a molecular-flow leak to the analyzer tube of a modified General Electric mass spectrometer. Since the gaseous products to be analyzed are  $CO$ ,  $O_2$ , and  $CO_2$  with both  $O^{16}$  and  $O^{18}$  present, the masses of concern are: 28- $CO^{16}$ , 30- $CO^{18}$ , 32- $O_2^{16-16}$ , 34- $O_2^{16-18}$ , 36- $O_2^{18-18}$ , 44- $CO_2^{16-16}$ , 46- $CO_2^{16-18}$ , and 48- $CO_2^{18-18}$ .

## RESULTS

To label the complex with respect to time of formation, a 0.100 g. Graphon sample was heated to 300°C. and exposed to  $O_2^{16-16}$  at a pressure of 0.490 Torr for a period of 2.5 hrs. At the end of this exposure, the  $O_2^{16-16}$  was removed and replaced with  $O_2^{18-18}$  (96.8 mole %  $O_2^{18-18}$ ) at a pressure of 0.435 Torr for a period of 6 hrs. Table I gives the analysis of the gas present after the two oxidation periods. The species  $O_2^{16-18}$  and  $O_2^{17-18}$  are a consequence of the  $O^{16}$  and  $O^{17}$  in the original  $O^{18}$  sample.

TABLE I  
ANALYSIS OF OXYGEN AFTER EXPOSURE TO GRAPHON AT 300°C.

Species	2.5 hr. Exposure ( $O_2^{16-16}$ ) Concentration, mole %	6 hr. Exposure ( $O_2^{18-18}$ ) Concentration, mole %
$O_2^{16-16}$	98.1	0.01
$O_2^{16-18}$	-	1.27
$O_2^{17-18}$	-	1.10
$O_2^{18-18}$	-	95.6
$CO^{16}$	1.58	0.09
$CO^{18}$	-	1.52
$CO_2^{16-16}$	0.38	-
$CO_2^{18-18}$	-	0.32

The complex formed in this two-step reaction was removed in increments by heating the carbon at a series of temperatures between 300 and 900°C. Most of the complex was recovered as  $CO$ . Table II gives the cumulative amount of each isotopic species of  $CO$  removed, following outgassing up to and including selected temperatures.

TABLE II  
ISOTOPIC DISTRIBUTION OF CO IN OUTGASSING PRODUCT FOLLOWING  
INITIAL TWO-STEP REACTION OF GRAPHON WITH OXYGEN AT 300°C.

Temp., °C.	Press., Torr $\times 10^3$		Mole %, CO <sup>18</sup>
	CO <sup>16</sup>	CO <sup>18</sup>	
400	0.72	0.23	24.2
500	2.60	0.77	22.9
600	6.02	1.66	21.6
700	13.7	4.35	24.1
800	21.1	6.25	22.8
900	24.0	6.95	22.5

To determine the role played by the surface complex in the carbon-oxygen reaction, the Graphon sample was then heated to 575°C. and reacted with O<sub>2</sub><sup>18-18</sup> at a pressure of 0.032 Torr. After a period of 45 min., the reactor was evacuated and O<sub>2</sub><sup>16-16</sup> at a pressure of 0.041 Torr was introduced. During the second reaction, the mass spectrometer monitored the partial pressures of O<sub>2</sub>, CO<sup>16</sup> and CO<sup>18</sup>. Table III gives the amount of CO<sup>16</sup> and CO<sup>18</sup> at various times of reaction. After 45 min., the reactor was evacuated and most of the complex that remained on the surface was removed by heating the Graphon to a temperature of 900°C. The CO resulting from the complex contained 53% CO<sup>18</sup>.

TABLE III  
ISOTOPIC DISTRIBUTION OF CO PRODUCED DURING REACTION OF  
O<sub>2</sub><sup>16-16</sup> WITH GRAPHON AT 575°C.  
IMMEDIATELY FOLLOWING REACTION OF O<sub>2</sub><sup>18-18</sup> WITH GRAPHON AT 575°C.

Time, min.	Pressure, Torr $\times 10^3$		Mole %, CO <sup>18</sup>
	CO <sup>16</sup>	CO <sup>18</sup>	
5	0.55	0.02	3.5
10	0.98	0.07	6.7
15	1.33	0.12	8.6
20	1.70	0.18	9.6
25	2.06	0.23	10.0
30	2.39	0.28	10.5
35	2.62	0.32	10.9
40	2.86	0.35	10.9
45	3.09	0.38	11.0

#### DISCUSSION

At any given temperature, a certain amount of surface complex will remain on the carbon surface. This effect (a varying activation energy of desorption) could be due to the nature of the carbon surface or the extent of surface complex coverage. If the changing activation energy of desorption is due to the nature of the carbon surface, that is, if there is a distribution of site activity, one would expect the strong sites to be the first to chemisorb oxygen and to require the highest temperature to release the oxygen in the form of CO. However, if the activation

energy for desorption is a function of the amount of complex remaining on the surface at that particular moment, one would not expect to find a relationship between time of adsorption and temperature of desorption.

The results of the decomposition of the surface complex formed at 300°C., as given in Table II, support the latter reason for a changing activation energy of desorption with coverage. This complex was produced by first exposing the Graphon sample to  $O_2^{16-16}$  for a period of 2.5 hrs. and then  $O_2^{18-18}$  for 6 hrs. It is seen that the concentration of  $CO^{18}$  in the decomposition products is about 23 mole % throughout the entire outgassing period, indicating that the time of formation of the surface complex has little effect upon the temperature (its activation energy) of removal.

Table I gives the composition of the oxidizing gas at the end of a 2.5 hr. reaction period ( $O_2^{16-16}$ ) and a 6 hr. reaction period ( $O_2^{18-18}$ ). Even though there was a relatively large amount of  $O^{16}$  surface complex present during the time of the  $O_2^{18-18}$  exposure, a negligible amount of  $CO^{16}$  was produced. This indicates: (1) that the oxygen in the gaseous CO produced during the reaction of  $O_2$  with Graphon came almost entirely from the  $O_2$  reacting at that instant and not from oxygen which had previously gone into a surface complex and (2) that there was little carbon monoxide-complex interaction.

In the 575°C. reactions, the first run with  $O_2$  produced an  $O^{18}$  complex. This complex was not removed prior to the  $O_2^{16-16}$  run. Since the  $O^{18}$  complex will behave in the same manner as the  $O^{16}$  complex, the amount of  $O^{18}$  appearing in the gas phase as  $CO^{18}$ , during the  $O_2^{16-16}$  reaction, affords a direct measure of complex decomposition. Therefore, the amount of  $CO^{18}$  in the gas phase is an indication of the effectiveness of the complex as an intermediate in the reaction, eg.



Table III gives the concentration of  $CO^{18}$  in the products of the  $O_2^{16-16}$  reaction. It is seen that the contribution of  $CO^{18}$  to the product gases increases as the reaction proceeds. This result is contrary to what would be expected if CO was predominately being produced through reaction (2). If this were the case, the  $CO^{18}$  in the total CO produced would have been a maximum at the beginning of the reaction of Graphon with  $O_2^{16-16}$ , when the  $O^{18}$  complex on the Graphon surface was at a maximum and the  $O^{16}$  complex was at a minimum. However, the increasing concentration of  $CO^{18}$  in the gas phase as the reaction proceeds indicates that the complex plays an increasingly important role in the production of CO. As the coverage of  $O^{16}$  complex increases (the  $O^{16}$  complex amounted to 47% of the total complex remaining after the  $O_2^{16-16}$  reaction), the activation energy of desorption of both the  $O^{16}$  and  $O^{18}$  complex becomes less. As a result, CO production by reaction 2 becomes significant.

At the end of the  $O_2^{16-16}$  reaction, most of the complex which had formed was removed by heating at 900°C. Throughout its removal, the  $CO^{18}$  concentration remained constant (53 mole %), again indicating no differentiation of the  $O^{18}$  and  $O^{16}$  complex as a result of its time of formation.



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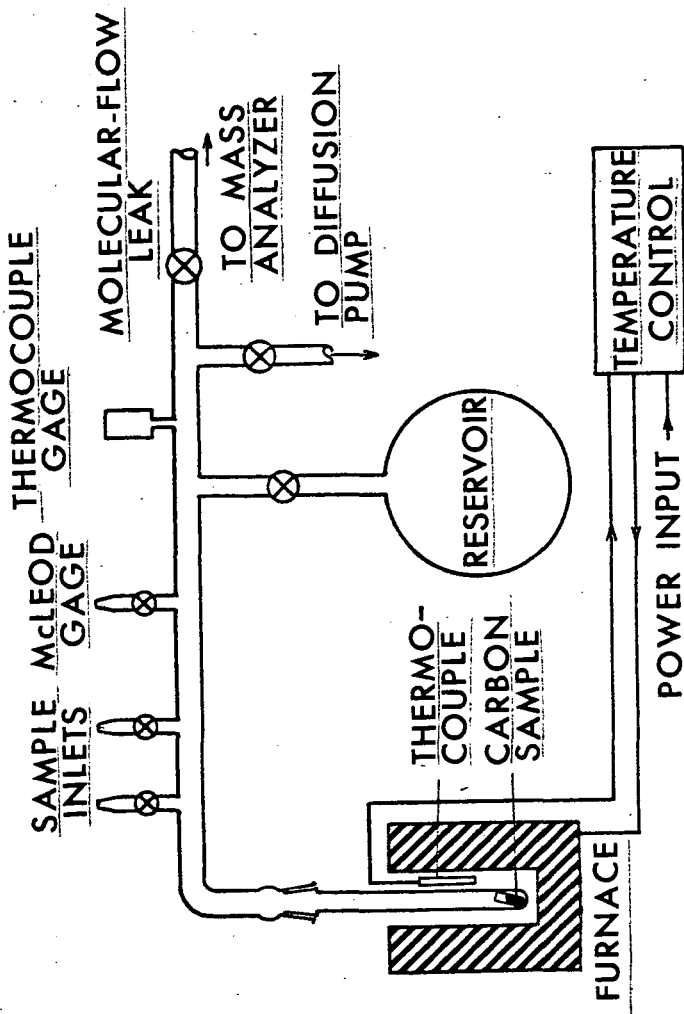


Figure 1. REACTOR

## THE USE OF SHORT HALF-LIFE RADIOISOTOPES IN TAGGING COAL

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An important use of radioisotopes in research on coal processing and coal research is in tagging the coal to determine the path it takes through the process under investigation. The application of radioactive tagging, however, is often limited by radiation hazards, process contamination, or the expense of radiation facilities. Although only a small amount of radioactive material is initially required to tag the material, equipment may soon become contaminated, decreasing the sensitivity of measurement and requiring successively larger amounts of radioactivity for subsequent tests. In addition, the product is often contaminated and there is the problem of disposal of radioactive materials. From a practical viewpoint a method is needed which is simple, accurate, completely safe and economical.

The use of short-lived radioisotopes having a half-life of perhaps one hour would solve these difficulties. However, this also introduces the problem of supplying such an isotope in useable form. The use of gamma "cows" or "milkers" solves this problem.

Method of Tagging Coal with a Short-Lived Radioisotope. One of the great advantages of radioactive tracers in industrial applications is the use of tracers with half-lives of one hour or less. This means that a few hours after they are used the radioactivity has completely disappeared. Such a tracer can be used without contaminating equipment or leaving any residual radioactivity. Since the radioactivity of short-lived tracers dies out in less than a day, however, one problem with them is a source of supply. This has been solved by the use of gamma "cows" or "milkers," including a means of separating the parent-daughter isotopes. In this method, a longer-lived parent element is stored for future use, then, when needed, the short half-life daughter element is separated or milked from the parent and used to tag the process material.

An example of a gamma cow is the element germanium-68 which is available in millicurie amounts as germanium chloride dissolved in about 20 ml. of dilute acid. The continuously produced daughter-isotope gallium-68 can be extracted as gallium chloride from the parent and used immediately. Germanium-68, the parent radioisotope, has a half-life of 250 days and can be used as a source of gallium-68 for several years before the activity of the germanium-68 becomes too low for use. During these years, the germanium can be extracted for gallium every ten minutes or as needed.

The extraction or milking procedure is very simple. Twenty milliliters of 25 percent acetylacetone are added to the germanium solution in a separatory funnel, shaken vigorously and allowed to clarify. Most of the acetylacetone solution, which contains only the daughter gallium, is decanted or withdrawn with an automatic pipette, leaving all of the germanium solution for subsequent extractions. The gallium solution can now be added to powdered coal, dried, and the tagged coal used immediately. The gallium solution can be injected directly into a pipeline, or if miscibility with water is required, the gallium may be extracted with an aqueous solution. Gallium-68, with a half-life of about one hour, emits both beta and gamma radiation. Its gamma radiation has an energy of 1.1 Mev, which means it can be effectively measured through an iron pipe or at a distance of several feet.

Nearly 1 millicurie of gallium can be obtained by each extraction from a stock of 2 millicuries of germanium. This provides enough radioactivity for most tracer applications. Regardless of how the short-lived gallium is used, it naturally disintegrates in a few hours forming stable zinc-68.

Use of Coal Tagged with Gallium-68. Gallium-68 is particularly useful in short-duration measurements of flow paths, flow rates, mixing operations, etc., which are completed in a few hours, and where contamination of product or equipment must be avoided. The tagged material can be added to a process stream with complete assurance that all radioactivity will be gone the next day.

Coal particles have been tagged with gallium-68 to measure reaction time of the coal and steam in a laboratory-scale coal gasifier. This gasifier is based on the falling particle technique (1) and is used to determine the reaction rate of pulverized coal as it drops through a steam atmosphere inside a 3-inch-diameter, 9-foot long tube at temperatures from 1,800 to 2,400° F. One of the problems with this apparatus is the accurate measurement of residence or contact time between the coal and the steam. The actual contact time was measured by adding slugs of tagged coal to the feed stream and measuring the time interval as these slugs passed radiation detectors located outside the gasifier at each end of the isothermal zone. The tagged coal was prepared by adding a few milliliters of the extracted gallium solution to a few grams of coal and drying in a heated test tube. The gallium was extracted and dried on the coal within 5 minutes, producing about 1 millicurie of radiation ( $3.7 \times 10^7$  disintegrations per second).

Figure 1 illustrates this application. The tagged coal passes two scintillation crystal detectors connected through ratemeters to a recorder. Each time the tagged coal passes a detector, gamma radiation from the coal produces a peak on the tracing. The contact time is a function of the distance between these peaks. Reproducibility of measurement for contact times of 3 to 10 seconds is 2 percent.

Most of the gallium chloride remains in the ash residue collected at the bottom of the gasifier. With successive measurements, the gallium-68 contaminates the system, causing an increase in the background count and reducing the accuracy of measurement. When this happens, the system is shut down until the next day when all of the radioactivity will have completely disappeared.

This method has been used repeatedly to measure the residence time of a variety of coals with far greater accuracy than other methods of measurement. Moreover, the method gave qualitative information on the mixing of coal and steam and pinpointed the location of an unexpected holdup in the residue collector.

Adaptations of this method are being used in other applications. One of these is the measurement of the slippage of solids entrained in liquid and gaseous media moving at high velocities. Here, a high-speed recorder measures the speed of tagged material to thousandths of a second.

## DISCUSSION

Germanium-68-gallium-68 is only one of many parent-daughter radioisotopes which can be used for a continuing supply of short half-life tracers. However, only a small number of these have practical significance from the standpoint of availability and appropriate decay characteristics. A cesium-137-barium-137 pair is commercially available as an automatic mechanical unit (2). The decay of tin-113 to indium-113m has been reported suitable for this use (3). Others include strontium-90-yttrium-90, tellurium-132-iodine-132, and molybdenum-99-technetium-99m (4).

The advantages of using gallium-68-germanium-68 for short half-life tracer applications are:

1. Application is completely safe and almost foolproof. Once the simple extraction of gallium from germanium has been made, the short-life gallium may be used in any process with complete assurance that no radioactivity will exist after a few hours. The main safety precaution is avoiding carry over of germanium in the gallium solution during extraction. We have found no trace of carry over using various techniques of extraction.
2. Only a small amount of radioactivity is needed even for repeated testing in the same unit. Since any contamination of equipment completely disappears in a few hours, there is no increase in background count after successive days and weeks of use.
3. There is no waste disposal problem beyond simply waiting a few hours.
4. The simple extraction of gallium from germanium can be completed in a few minutes and the short-lived product used to tag almost any solid or liquid material, either as a water or oil solution. A junior chemist, or chemical technician, should find this to be a simple procedure.
5. The short-life gallium is a strong gamma emitter; tagged materials can be detected through heavy-walled pipes or at distances of several feet.
6. A formal radioisotope laboratory is not required for this method, since the amount of radioactivity needed for most applications is very low; 1 to 2 millicuries of germanium is adequate for most applications. The extraction of gallium from germanium should be performed in a chemical hood. Beyond a portable survey meter and proper shielding or storage place for the separatory funnel of germanium, no special facilities are needed. As germanium-68 is a cyclotron-produced radioisotope, a license from the Atomic Energy Commission is not required. A potential user must only satisfy the supplier that he has the minimum instruments needed for safe usage. In our use of this method of tagging coal, the total personnel exposure was calculated to be less than 1 millirad per month; film badges and dosimeters did not show any exposure.

The disadvantages of this method largely depend on the application:

1. Large amounts of germanium-68 are not readily available. Cyclotron production is usually in millicurie quantities, so that the applications of gallium-68 are generally limited to laboratory and pilot-scale applications. For determining the flow rate in a heavy-walled pipeline, a millicurie of germanium is adequate but this method is not suitable for applications requiring large amounts of radioactive material.
2. Because of the short half-life of gallium-68, the actual measurement must be completed in less than an hour, or before the radioactivity drops too low to measure. This also limits the sample preparation time. However, the availability of 1 millicurie of gallium from 2 millicuries of germanium every half-hour permits wide experimentation in methods of sample preparation.

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USE OF COAL TAGGED WITH RADIOACTIVE GALLIUM - 68 IN BUREAU OF MINES RESEARCH

FIGURE 1

## IRRADIATION DOES NOT ALTER THE PARTICLE SIZE OF COAL

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The size reduction of coal is of considerable interest, both fundamentally and commercially, because it makes a larger surface area available for chemical reaction. Also, several potential coal processes are limited, directly or indirectly, by the abrasiveness of coal or coal ash particles moving at high velocities. For example, blades in a coal-burning gas turbine would probably be subject to less wear whenever agglomeration of the ash from micron size coal is avoided during combustion. Many new uses for coal can be envisioned if micron-size coal can be produced economically.

The irradiation of coal with gamma rays has been reported (3) to result in considerable particle size reduction. On the other hand, many coal irradiations have been made without the investigators noticing any significant particle size reduction, although the effect of irradiation on particle size was not closely examined.

Because of the possible economic significance with respect to the size reduction of coal, the Bureau of Mines began work at the Morgantown Coal Research Center to determine the magnitude of this effect.

Since a considerable number of variables could affect the size reduction of coal particles, a qualitative survey was made first on relatively small samples irradiated at low flux. After successive irradiations gave negative results, quantitative tests were later made on larger samples irradiated at higher flux.

Irradiation of Small Samples at Low Flux. Coals irradiated at low flux included lignite, from the Lehigh bed, Stark County, N. D.; subbituminous B coal, from the Adaville No. 1 bed, Elkol Mine, Wyoming; high-volatile C bituminous coal from the No. 2 bed, Wilmington Mine, northern Illinois; strongly coking high-volatile A bituminous coal from the Sewickley bed, Bunker Mine, Monongalia County, W. Va.; anthracite, from the middle bench of the Bottom Ross Seam, Glen Alden Mine, Wilkes-Barre, Pa.; and an unidentified coking-type bituminous coal.

These coals were irradiated at the Radcell Facility, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tenn. Approximately 6-gram samples of each of the first five coals were sized and irradiated, with and without predrying, for various periods of time. Also, several size-ranges of one coal, the subbituminous B, were irradiated. The sixth coal, the unidentified coking-type bituminous coal, was irradiated in lump form of 1/4-to-1-inch pieces. All samples were placed in stoppered glass vials and irradiated with a Co-60 source at an hourly gamma dose rate of about  $2 \times 10^7$  ergs per gram (reference to carbon). (One erg per gram equals 0.0114 roentgen.) Untreated samples of each were retained for comparison. Since only qualitative effects were being determined, no particular care was taken in sampling each lot.

The particle sizes of the irradiated and untreated coal samples were determined by the Palo-Travis sedimentation method (4). This method is accurate to 15 microns for comparing the size distributions of similar samples.

Results of the qualitative tests are shown in Table 1. The variables in this table are (a) ranks of coal from lignite to anthracite; (b) sizes from lumps to 200-230 mesh particles; (c) dried and undried coal; and (d) radiation exposure times of 2 hours to 10 days. In no case was there any evidence of a significant reduction in the size of the coal particles. There is some random scatter of data because of the difficulty of handling small samples of powdered coal without segregation of sizes. However, the difference in size of the irradiated and untreated coal fell within the accuracy of the size-determination method. The coal that had been irradiated in lump form was examined under a microscope but there was no visible evidence of any physical change.

Irradiation of Large Samples at High Flux. Since the preliminary investigation failed to reveal any definite indication of particle size reduction, a quantitative investigation was undertaken. In this work, relatively large amounts of coal were irradiated at very high flux levels and the particle-size distributions of the product were determined by several methods.

Sample Preparation and Irradiation. Three pounds each of lignite from the Lehigh bed, Stark County, N. D., and high-volatile C bituminous coal from the Rock Springs bed in Wyoming were irradiated in separate alloy-steel cylinders. The irradiations were performed at the National Reactor Testing Station, Idaho Falls, Idaho, with spent MTR fuel assemblies as sources of high-intensity gamma radiation (1).

Each sample of coal was pulverized and screened three times on a Rotap shaker by the A.S.T.M. method to insure that the sample was within the size range specified---minus 200 - 230-mesh U. S. Standard Sieve Series. A small sample of minus 90 - plus 120-mesh lignite was also prepared. After sizing, each coal was carefully mixed and quartered into duplicate samples, separately wrapped and placed in identical cylinders. The duplicate samples were prepared so that the irradiated coal could be compared with untreated coal that had received the same preparation and handling procedure. Each cylinder was evacuated, purged three times with helium and evacuated for 3 days to an absolute pressure of 180 microns of mercury. Helium was then admitted into each cylinder until a gage pressure of 2 inches of mercury was attained. The cylinders were then sealed.

The cylinders were irradiated for 308 hours at a flux rate of about  $3 \times 10^8$  ergs per gram per hour. The average total dosage of each sample was as follows:

High volatile C	-200 + 230 mesh	$7 \times 10^{10}$ ergs g <sup>-1</sup> (c)
Lignite	-200 + 230 mesh	5 ditto
Lignite	-90 + 120 mesh	6 ditto

Methods of Size Analysis and Results. The irradiated and untreated coals were analyzed for particle-size distribution to determine any changes in size because of irradiation. Since there is no widely accepted method of size analysis of coal, the sizes of the irradiated and untreated coal were determined in several different ways. These included the Palo-Travis sedimentation method, a standard sieve analysis using a Rotap shaker, a microscopic method of direct counting, and the Coulter method of analysis.

Figure 1 shows typical particle-size distribution curves for duplicate tests of irradiated and untreated samples of the high volatile C bituminous coal. These curves were obtained by the Palo-Travis sedimentation method (4). As determined from the integrated area below these curves, the average particle sizes of the irradiated and untreated coals were 70 and 74 microns, respectively. This difference in size is not significant. Even if irradiation reduced the size of a small amount of the particles, the curve would "tail-off" much more in the direction of the smaller particle sizes. As can be seen, however, the size distributions of the irradiated and untreated samples are remarkably similar.

TABLE 1. - Results of Irradiating Small Samples of Pulverized Coal

Type of coal	Original size range, U. S. standard sieve <sup>1/</sup>	Exposure time, days	Average size by sedimentation method, microns
Lignite, untreated	-90 + 120	0	169
Lignite	-90 + 120	1	189
Lignite	-90 + 120	3	189
Lignite, dried	-90 + 120	1	182
Subbituminous B, untreated	-40 + 45	0	378
Subbituminous B	-40 + 45	3	390
Subbituminous B, dried	-40 + 45	1	343 <sup>2/</sup>
Subbituminous B, untreated	-90 + 120	0	176
Subbituminous B	-90 + 120	3	169
Subbituminous B, dried	-90 + 120	1	169
Subbituminous B, untreated	-200 + 230	0	81
Subbituminous B	-200 + 230	2 hrs.	81
Subbituminous B	-200 + 230	10	81
Subbituminous B	-200 + 230	1	81
High volatile A, untreated	-90 + 120	0	158
High volatile A	-90 + 120	1	166
High volatile A	-90 + 120	3	161
High volatile A, dried	-90 + 120	1	160
High volatile C, untreated	-200 + 230	0	88
High volatile C	-200 + 230	1	87
High volatile C	-200 + 230	3	88
High volatile C, dried	-200 + 230	1	90
Anthracite, untreated	-90 + 120	0	126 <sup>2/</sup>
Anthracite	-90 + 120	1	150
Anthracite	-90 + 120	3	151
Anthracite, dried	-90 + 120	1	138
Coking bituminous	lump	10	unchanged

<sup>1/</sup> Various coal types of the same original size-range may differ in average size (shown in column 4) because of different methods of screening.

<sup>2/</sup> Probably in error; test could not be repeated owing to insufficient sample.



The same equipment used to size the original coal was used to make sieve analyses of the irradiated and untreated coals. The results are shown in Table 2. No significant particle-size reduction is apparent.

TABLE 2. - Size analysis of irradiated and untreated coals by sedimentation and sieve methods

Type of coal	Average size by sedimentation method, microns	Sieve analysis <sup>1/</sup>		
		+200	-200 + 230	-230
High volatile C				
Irradiated	70	7.5	82.1	10.4
Untreated	74	11.6	82.0	6.4
Lignite				
Irradiated	99	8.2	80.3	11.5
Untreated	99	7.4	78.4	14.2
		+ 90	- 90 + 120	-120
Lignite				
Irradiated	167	0.8	87.4	11.8
Untreated	166	.5	85.5	14.0

<sup>1/</sup> Weight-percent shown with each indicated mesh-size.

A microscope method of size analysis also was used. In this method, the actual number of particles in each size range is counted (2). Table 3 shows a typical size analysis of the high volatile C bituminous coal. The results showed there was no alteration in particle size due to irradiation.

TABLE 3. - Size analysis by microscope count method of irradiated and untreated high volatile C bituminous coal

Particle size, microns	Percentage by count		Percent by volume	
	Irradiated	Untreated	Irradiated	Untreated
0-2	73.90	59.82	0.01	0.01
2-5	21.84	36.42	.15	.31
5-10	.70	.82	.05	.07
10-20	.11	.14	.06	.10
20-40	.40	.42	1.72	2.22
40-60	2.10	1.63	41.46	40.04
60-80	.81	.60	43.79	40.51
>80	.14	.15	12.76	16.74

The Coulter method of analysis was also used to determine the particle-size distributions of the irradiated and untreated Rock Springs coal. The size distributions are shown in figure 2. Again there is no indication of any difference in particle sizes of irradiated and untreated coal. It is interesting to note the similarities of the size distributions determined by the sedimentation method (figure 1) and those determined by the Coulter method (figure 2).

Irradiation of Bituminous Coals of the Same Rank. Although irradiation of coals of different rank did not reveal any indication of significant size reduction, the possibility remained that some other coal within the same rank might be affected by irradiation. The coal previously reported to have been reduced in size by means of irradiation was a high-volatile C bituminous coal from the Kenilworth seam in Utah. Accordingly, samples of the Kenilworth coal and two other bituminous coals of the same class---a low-volatile bituminous coal from the Pocahontas No. 3 bed, W. Va., and a high-volatile A bituminous coal from the Pittsburgh seam, Bruceton, Pa., ---were prepared and irradiated at the National Reactor Testing Station as described previously.

The average total gamma dose given each coal was  $5 \times 10^{10}$  ergs per gram (reference to carbon). Following irradiation the size of each irradiated coal was determined by each of the four methods previously used. In no case was there any indication of size reduction.

A fifth method of size comparison was made with the Kenilworth coal. Part of the irradiated and untreated Kenilworth coal was returned to the supplying organization, the Denver and Rio Grande Western Railroad Company. This company compared the two samples by photographing the coals with an electron microscope at a magnification of 50. Figure 3 shows the electron photomicrographs of the irradiated and untreated Kenilworth coal. The photomicrographs do not reveal any difference in particle size.

#### DISCUSSION

The tests conducted by the Bureau of Mines show that irradiating coal with gamma rays does not change the size of the particles. Errors due to segregation and sampling of pulverized coal may cause apparent effects that might easily be attributed to irradiation effects. Casual inspection of the data in Table 1, for instance, might lead to a conclusion that irradiation slightly altered the size of anthracite. Subsequent irradiations with careful sampling, however, showed there was actually no significant change in particle size.

Several coals irradiated with neutrons were visually inspected and revealed no apparent change in size, but the induced radioactivity of the ash in the coal precluded more detailed examination.

An attempt was made to measure the increase in hardness of irradiated coals by determining the difference in grindability. Small samples of irradiated and untreated coal were ground in a ball mill for equal periods of time and the size distribution of each coal compared. The accuracy of this method was quite poor, reproducibility of the method being about 10 percent. Within these wide limits, there was no significant difference between grindability of gamma irradiated and untreated coal. The results suggest that if irradiation increases the hardness of coal, the increase in grindability must be less than 10 percent.

#### ACKNOWLEDGMENTS

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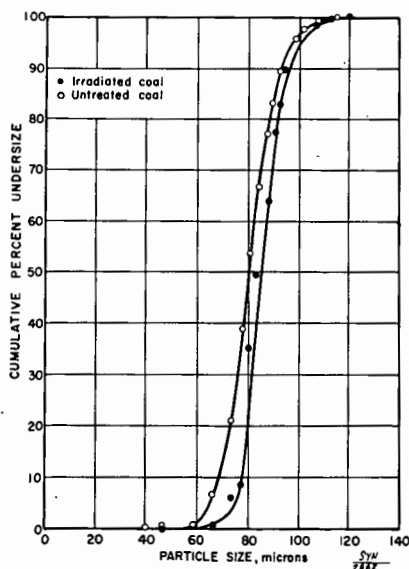
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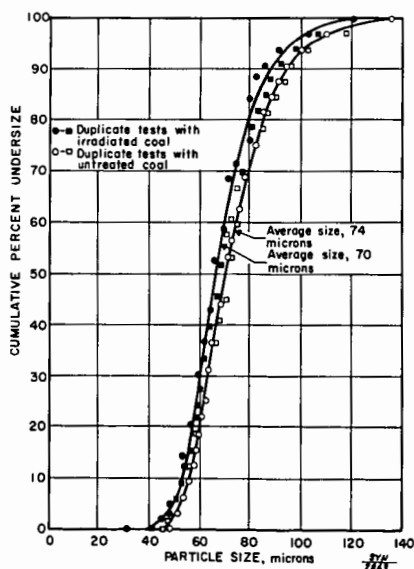
Electron Photomicrographs of Untreated and Irradiated  
Kenilworth Coal  
Composite Photograph Courtesy of the Denver and Rio  
Grande Western Railroad Co.

FIGURE 3



SIZE DISTRIBUTION CURVES OF IRRADIATED AND  
UNTREATED HIGH VOLATILE C BITUMINOUS COAL,  
AS DETERMINED BY THE COULTER METHOD

FIGURE 2



TYPICAL SIZE DISTRIBUTION CURVES OF IRRADIATED  
AND UNTREATED HIGH VOLATILE C BITUMINOUS COAL,  
AS DETERMINED BY THE PALO TRAVIS SEDIMENTATION METHOD

FIGURE 1